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C. E. Beecher.

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

CHARLES EMERSON BEECHER.

One of America's leading paleontologists, in the fullness of intellectual power, suddenly passed away on February 14, 1904, in the midst of his family and work. Few men were better prepared and more promising of great results for the next twenty years than Charles E. Beecher. "There is no doubt that in the death of Professor Beecher, not only has Yale sustained a serious loss and paleontology a severe blow, but the ranks of those capable of bringing to the study of fossils keen insight and a philosophical spirit of enquiry, guided by principles whose value can hardly be exaggerated, are diminished by one whom science could ill afford to lose, and to whom, humanly speaking, there should have remained many years of industry and fruitful research." (W. H. Dall, Science, March 18, 1904.)

Like most successful students of organic life, Beecher was a born naturalist. As a boy of twelve years he began to make a collection of recent shells and fossils, continuing to add to this for the next thirty years, when, in 1899, he presented Yale University, "unconditionally," with upwards of 100,000 fossils. In the field few excelled Beecher as a collector. When twenty years of age he published his first paper—a list of the land and fresh-water shells of Ann Arbor, Michigan. For the next eight years he published nothing, his second paper appearing in 1884, and in 1888, when he left Albany,

there were but twelve papers to his credit. Since that time, during the years spent at New Haven, he has written fifty-eight articles, making a total of seventy numbers in his bibliography. As a paleontologist he began by describing species and genera, but later he took almost no interest in this kind of work. Often he told the writer that he wished all our fossils were named. Of faunal and stratigraphic papers he has five, and of new species he described but thirty-six. He defined nine new genera and seven new orders. During the past fifteen years his mind was absorbed in working out the ontogenetic stages in fossil species and in tracing their genetic sequence through the geological formations. To Beecher we owe the first natural classification of the Brachiopoda and Trilobita, based on the law of recapitulation and on chronogenesis. He also gave a very philosophic account as to the origin and significance of spines in plants and animals. On these works his reputation in days to come will chiefly rest.

Beecher was not only a born naturalist but also had much mechanical ability. Nothing pleased him more than to free fossils from the surrounding matrix, and his unexcelled talent in this direction is shown in the preparations of *Triarthrus* and *Trinucleus* in the Yale University museum. More than 500 specimens have been prepared by him and this work has required peculiar skill, patience, ingenuity, and a great deal of time. Few can appreciate Beecher's remarkable talent in cleaning the adhering black shale from these small specimens, and it will be a long time before another will be found who can equal him in this respect. It is very unfortunate that he did not live to complete his studies on the trilobites, but he left all the better specimens completely worked out, and of most of these he had made photographs and drawings. His mechanical bent was also evidenced at his home, where he had a bench and a large kit of tools. Here his diversion consisted in making brass scrolls, shelves, and delicately carved boxes and chests. His preparations for the microscope, also, are of the best, and much time in his earlier years was spent in freeing and mounting the lingual dentition in small species of living gastropods. He likewise modeled and made a life-size restoration of the Devonian giant *Stylonurus*.

After Beecher's appointment as Curator of the geological collections at Yale, he also undertook to arrange, develop, and place on exhibition the large Marsh collection of vertebrates. His work in this connection, however, was chiefly directive, although he assisted considerably in the mechanical work of the large mounts of *Claosaurus annectens* and *Brontosaurus*. The life-like poses selected for these specimens are evidences of his artistic perception. The former he has described at length in the Transactions of the Connecticut Academy.

Charles Emerson Beecher, son of Moses and Emily D. Beecher, was born in Dunkirk, New York, October 9, 1856. Not long after this date, his parents removed to Warren, Pennsylvania, where he prepared for college at the High School, and was graduated from the University of Michigan, receiving the degree of B.S. in 1878. The ten succeeding years he served as an assistant to Professor James Hall, and in 1888 removed to New Haven to take charge of the collections of invertebrate fossils in the Peabody Museum. His career as a teacher of geology began in 1891 when for two years he took charge of Dana's classes at Yale, and in 1892 he was made Assistant Professor of Historical Geology in the Sheffield Scientific School, serving in this capacity until 1897 when he became Professor of Historical Geology and a member of the Governing Board in the Sheffield Scientific School. In 1899 he succeeded the late Professor Marsh as Curator of the geological collections, and was made a member of, and secretary to, the Board of Trustees of the Museum. In 1902 his title was changed to that of University Professor of Paleontology. He was eminently successful as a teacher both with undergraduates and with advanced students, his enthusiasm and kindliness of character arousing at once their interest and devotion.

Professor Chittenden, director of the Sheffield Scientific School, has said of Beecher: "Quiet and unassuming he never sought adulation, but where there was earnest work to be done, requiring skill, patience and good judgment, he would labor quietly and industriously, bringing to bear upon the problem such a measure of common sense and of thoughtfulness that confidence and respect for his conclusions were inevitable.

. . . . . As a friend he was loyal and trustworthy, and his memory will always be cherished by his associates in the Sheffield Scientific School with a full realization of the great loss they have sustained in his removal from their midst, and with an equal realization of the great loss to the institution to which he was so ardently devoted and in the future of which he had such great confidence."

Beecher received the degree of Ph.D. from Yale in 1889, his thesis being a memoir on the Ordovician Brachiospongidæ. In 1899 he was elected a member of the National Academy of Sciences, a foreign correspondent of the Geological Society of London, and a fellow of the Geological Society of America. In 1900 he was elected President of the Connecticut Academy of Arts and Sciences, and filled this office for two years. He was also a member of the American Association of Conchologists, Geological Society of Washington, Boston Society of Natural History, and Malacological Society of London.

Beecher's first paleontologic paper was published by the Geological Survey of Pennsylvania in 1884, when he was twenty-eight years old. It treated of new genera and species of Phyllocarida from the Devonian, a group of rare Crustacea, most of which he had found about his home. He was always on the lookout for these rare fossils, and after securing many hundred additional specimens, he again returned to the subject, and in 1902, in a paper published by the Geological Society of London, embodied all that is known of the Upper Devonian Phyllocarida of Pennsylvania.

If, during the past ten years, Beecher's time had not been so much taken up with trilobites, he probably would have worked out a phylogenetic classification of the corals. In 1891 he published two important papers on paleozoic corals, one based on *Pleurodictyum lenticulare* and the other on *Michelinia convexa*. He concluded that poriferous corals begin with a simple cyathiform corallite, without mural pores, and with septa first appearing toward the end of this stage. These features "indicate a primitive, simple, and imperforate ancestry for the Perforata." The next stage is suggestive of *Aulopora*, and the final stage in *P. lenticulare* has at least seven mural pores open-

ing into the primary calyx. In regard to the mural pores, he concluded from a study of them in *Favosites*, *Striatopora*, *Pleurodictyum*, and *Michelinia*, that they "are ineffectual attempts at budding, resulting only in the perforation of the cell walls."

In his third paper on corals he states that a specimen of *Romingeria umbellifera* measuring 100×200^{mm} has approximately 1500 corallites on each zone, or 4500 on the three zones. In 85 per cent of individuals each corallite gives rise to twelve buds, so that if each of the 1500 corallites of the basal zone give rise to twelve buds, there should be on the third zone 253,500 corallites. However, as there are only 4500 in the specimen in the three zones, "this shows a suppression of 243,000 corallites on two zones."

Beecher's first turn from stratigraphic paloentology to pure paleo-biology and correlation had its origin in the brachiopods. While at Albany he became acquainted with Hyatt's principles, although it was not until he had been some years at New Haven that he fully appreciated their application to fossils. Hall had made large collections of the Silurian fossils at Waldron, Indiana. This collection contained many slabs, and, as much loose clay adhered to them, Beecher saved the washings and out of these he and Clarke obtained about 50,000 specimens of young brachiopods. Their results were published in 1889 in a well-illustrated paper entitled "Development of some Silurian Brachiopods." In summing up the developmental changes, they made the following very significant statement: "In nearly every species the inceptive state is represented by a shell having a subcircular outline, with valves of slight convexity. This phase usually disappears before the individual reaches a length of 1^{mm}, after which the specific characters are assumed." Widely differing species "are alike in form, contour, convexity, beaks, and cardinal area, and the only marked differences are to be found in the faint indications of plications, striæ, folds and sinuses."

From a study of the nature of the pedicle opening they concluded that the "phylogenetic development tended in two main channels—one leading through *Strophomena*, *Scenidium*, *Orthisina*, *Leptæna*, *Chonetes*, *Productus*, and *Strophalosia*, and the other in the direction of *Rhynchonella*, *Spirifer*,

Atrypa, *Retzia*, and *Terebratula*." It will be noticed that this arrangement of widely differing genera foreshadows two orders of brachiopods for which Beecher later proposed Neotremata and Telotremata.

My acquaintance with Beecher began in 1889, and at that time it was evident that the paper just referred to was being considered with a better understanding of what Hyatt's principles meant when applied to Brachiopoda. The very fact that nearly all the Waldron, Indiana, brachiopods began with smooth shells having a subcircular outline, led him to look for this early stage in other genera, but as no other young shells were at hand, he resorted to a study of the beaks in well-preserved examples of mature shells. During the fall of 1890 he spent nearly a week going through my collection, and with studies made on other collections he was able to announce in the spring of 1891 that he had seen the initial shell in fifteen families as recognized by Œhlert in Fischer's "Manuel de Conchyliologie," these being represented by forty genera.

At this time he made the important announcement "that all brachiopods, so far as studied by the writer, have a common form of embryonic shell, which may be termed the *protegulum*." The protegulum is the phylembryonic stage of Brachiopoda. A prototype preserving throughout its development the main features of the protegulum was at first supposed to exist in the Lower Cambrian *Paterina*, but as this proved to be identical in structure with *Iphidea*, the conclusion had to be abandoned. However, at maturity this genus is so closely related in general form with the protegulum, that we may hope at any time to find the prototype.

A study of the stages of growth in many brachiopods, from the Cambrian to the living forms, enabled Beecher to show that the old classifications based upon the presence or absence of hinge teeth, the nature of the intestinal canal, etc., were not expressive of genetic relationship. He demonstrated that on the basis of types of pedicle openings all brachiopods are naturally grouped into four orders, of which two are without and two possess hinge teeth. The most primitive order (*Lingula*, etc.) he named Atremata, and this gave rise directly to the Telotremata (*Rhynchonella*, *Terebratula*, etc.). The Neotremata (*Crania*, *Discina*, etc.) also originated in the Atremata,

and from the former descended the Protremata (*Strophomena*, *Productus*, etc.).

One of the clearest cases of parallelism between the ontogeny and phylogeny in a group of invertebrates was described by Beecher. Living species of the family Terebratellidæ have a very wide distribution, and he showed that the highest genera of the austral forms "pass through stages corellated with the adult structure in the genera *Gwynia*, *Cistella*, *Bourchardia*, *Megerlina*, *Magas*, *Magasella*, and *Terebratella*, and reach their final development in *Magellania*." In the forms having a boreal distribution the metamorphoses corellate "with adult structures of *Gwynia*, *Cistella*, *Platidia*, *Ismenia*, *Mühlfeldtia*, *Terebratalia*, and *Dallina*. The first two stages in both subfamilies are related in the same manner to *Gwynia* and *Cistella*. The subsequent stages are different except the last two, so that the *Magellania* structure is similar in all respects to the *Dallina* structure, and *Terebratella* is like *Terebratalia*. Therefore *Magellania* and *Terebratella* are respectively the exact morphological equivalents to, or are in exact parallelism with *Dallina* and *Terebratalia*.

"In each line of progression in the Terebratellidæ, the acceleration of the period of reproduction, by the influence of environment, threw off genera which did not go through the complete series of metamorphoses, but are otherwise fully adult, and even may show reversional tendencies due to old age; so that nearly every stage passed through by the higher genera has a fixed representative in a lower genus. Moreover, the lower genera are not merely equivalent to, or in exact parallelism with, the early stages of the higher, but they express a permanent type of structure, as far as these genera are concerned, and after reaching maturity do not show a tendency to attain higher phases of development, but thicken the shell and cardinal process, absorb the deltidial plates, and exhibit all the evidences of senility."

In 1893 there was discovered in the Utica formation near Rome, New York, a thin band not more than one-fourth of an inch thick, in which nearly all the fossils preserved (*Triarthrus* and *Trinucleus*) occur as pseudomorphs in iron pyrite, and retain antennæ and legs. Specimens of trilobites with legs had been known before in two specimens, and in four genera

the legs had been determined by slicing enrolled individuals. Antennæ, however, had not been clearly made out until 1893, when their presence was announced in the August number of this Journal. This discovery was of great value and promised much toward a better understanding of the ventral anatomy of trilobites and their systematic position among the Crustacea. This led to Beecher's visiting the locality in 1893 to take out several tons of the shale. Even as late as last fall he developed from this material specimens of *Trinucleus* showing the ventral appendages in the greatest detail. Since 1893 Beecher has published fifteen papers on the trilobites. Of these three are devoted to the larval stages, seven to the ventral anatomy, and five to classification and the systematic position of these forms.

The ventral anatomy is most completely known in *Triarthrus*, "an active creature" belonging to an ancient Cambrian family. Beecher showed that in this genus the entire series of thoracic legs are biramous, one of them setæ-bearing and used for swimming (expodite), and the other without setæ and used for crawling (endopodite). The limbs of the pygidium overlap each other, are much crowded, and are adapted for swimming or guiding the animal, although they may also have served as egg carriers. The individual segments "are considerably expanded transversely, thus making a paddle-like organ." The head has five pairs of appendages as follows: Anterior antennæ or uniramous antennules attached at the side of the hypostoma, followed by four pairs of biramous appendages closely resembling the thoracic legs. These are (1) posterior antennæ, (2) mandibles, (3 and 4) maxillæ. The ventral membrane of *Triarthrus* "is of extreme tenuity" and is an "uncalcified, chitinous, flexible pellicle, and thus was in strong contrast with the much thicker and calcified dorsal test."

The larval stages he studied in nine genera ranging from the Cambrian to the Lower Devonian. He concluded that "all the facts in the ontogeny of the trilobites point to one type of larval structure." This larva, not more than one millimeter in length, is "characteristic of all trilobites, and among different genera, varying only in features of secondary importance. This stage may therefore be called the *protaspis*." He found that Barrande's four orders of trilobite development are but stages of his first order, and that *Agnostus* is "neither

the phylo-typembryo nor the phylo-phylembryo, but is really the adult equivalent to an early segmented stage of the higher genera." Beecher divided the early stages of development in trilobites as follows: "Nauplius (Cephalon predominating, other parts not separated from it), Phylembryonic (Cephalon distinct, thorax nothing, pygidium distinct), Nepionic with as many stages as there are normal thoracic segments (Cephalon distinct, thorax incomplete, pygidium distinct), Neanic (Cephalon, thorax and pygidium all distinct and complete; growth incomplete), Ephebic (all parts complete and full size attained)."

The protaspis is homologous to the crustacean nauplius, which had "potentially five cephalic segments bearing appendages, which should therefore be taken as characteristic of a protonauplius. The nauplius is a modified crustacean larva. The protaspis more nearly represents the primitive ancestral larval form for the class, and approximates the protonauplius."

The basis for Beecher's classification of the trilobites is the application, for the first time, of the law of morphogenesis, or the recapitulation theory. He observed that in the first or unsegmented stage of the most primitive trilobites there are neither dorsal free cheeks nor eyes, but that in some of the later forms both the eyes and free cheeks have migrated to the anterior margin or may even have progressed a little posteriorly down the dorsal side of the protaspis. This led him to undertake a study of all trilobite genera, more than two hundred in number, and it was seen that these could be arranged in three groups on the basis of the nature and position of the free cheeks. In the most primitive order, or the Hypoparia, there are "free cheeks forming a continuous marginal ventral plate of the cephalon, and in some forms also extending over the dorsal side at the genal angles." In the Opisthoparia the dorsal "free cheeks include the genal angles, thus cutting off more or less of the pleura of the occipital segment;" while in the Proparia, or the last order to arise, "the pleura of the occipital segment extend the full width of the base of the cephalon, embracing the genal angles."

There is much diversity of opinion regarding the rank of trilobites in a classification of the Crustacea. Beecher regarded them as a sub-class and as equal in rank to the Entomostraca and Malacostraca. "In nearly every particular the trilobite is very primitive, and closely agrees with the theoretical crusta-

cean ancestor. Its affinities are with both the other sub-classes, especially their lower orders, but its position is not intermediate."

In 1892 Beecher became greatly interested in the significance of spines, accumulating data until 1898, when he presented his studies in a paper entitled "The origin and significance of spines." This paper Beecher regarded as his best and most philosophic work. In the opening paragraph he states "the presence of spines in various plants and animals is, at times, most obvious to all mankind, and not unnaturally they have come to be regarded almost wholly in the light of defensive weapons." "Their importance lies not in what they *are*, but in what they *represent*. They *are* simply prickles, thorns, spines, or horns; they *represent*, as will be shown, a stage of evolution, a degree of differentiation in the organism, a ratio of its adaptability to the environment, a result of selective forces, and a measure of vital power."

"In tracing the ontogeny of a spinose form, it has been found that each species at the beginning was plain and simple, and at some later period, spines were gradually developed according to a definite sequence of stages. Usually after the maturity of the organism, the spines reach their greatest perfection, and in old age, there is first an over-production or extravagant differentiation followed by a decline of spinous growth, and ending in extreme senility with their total absence."

He found that all kinds of spines in plants and animals can be arranged into eleven distinct categories. Further, that two generalizations result as follows: "That spinosity represents the limit of morphological variation, and second, it indicates the decline or paracme of vitality." "Finally it is evident that, after attaining the limit of spine differentiation, spinose organisms leave no descendants, and also that out of spinose types no new types are developed."

Beecher's standing among biologists and paleontologists was high; he was a leader among students of Brachiopoda and Trilobita. His paleontologic work at Yale was essentially of a biologic and philosophic character. He had the artist's gift, nearly all the drawings illustrating his various papers being made by himself and exhibiting a high order of merit. He

was a slow and very careful worker. Those who knew him well saw in him an enthusiast, but his exuberance was always held in check by his judicial qualities, which also made him an excellent counselor. He was orderly in his work, and, as he had the "museum instinct" well developed, he made one of the best of museum curators.

In 1894, Beecher married Mary Salome Galligan of Warren, Pennsylvania, who, with two daughters, survives him. He died very suddenly of heart disease at his home, shortly after one o'clock on Sunday afternoon, February 14. Up to about eleven o'clock of the same day, he was in his usual health. He lies in Grove Street Cemetery, in the shadow of the Sheffield Scientific School.

CHARLES SCHUCHERT.

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ART. XXXIX.—*Dinosaur Footprints from Arizona*; by E. S. RIGGS.

A SLAB of sandstone bearing dinosaur footprints, recently received at the Field Columbian Museum, is of interest in marking a new locality for these well-known fossils. The tracks were found in the bluffs overlooking the Colorado River,

Dinosaur tracks one-fourth natural size.

near Lees' Ferry in Northern Arizona. Mr. F. V. Kearn, the collector, reports that there were six impressions in all, but he succeeded in preserving only two. The matrix is a sharp, fine-grained sandstone of a bluff color when freshly broken, but weathering to a dark reddish brown. Data as to the geological horizon are wanting, but it may be assumed that the specimen is of Triassic age.

The impressions are evidently made by the hind feet of a tridactyl animal similar in structure to those of *Allosaurus* Marsh, but considerably smaller. The tracks preserved are but a few inches apart and were apparently made in wet sand. That of the right foot is barely its own length in advance of the left and is separated by a similar distance laterally. It may

therefore be inferred that the tracks were made by a bipedal animal walking leisurely along a sandy beach.

In outline the tracks are almost symmetrical to a line passed through the imprint of the middle digit. The axis of the foot is deflected but little from the line of stride. The middle digit was evidently strongest and bore more than an equal share of the animal's weight. The two lateral digits appear to have been equally functional and, like the middle one, were armed with claws. The inferior surface of the foot was provided with pads similar to those of struthious birds. In digit II the weight was borne upon the first and second phalanges, in digit III upon the second and third, while in digit IV the second, third and fourth were evidently brought to the ground. In addition to this there is an imprint of a heel-like pad which was borne by the distal ends of the metatarsals.

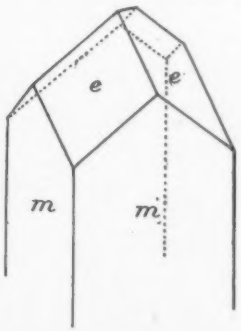
Measurements are as follows:

	M
Length over all	·128
Breadth	·103
Length of lateral digits from heel	·079
Angle between digits II and III	35°
" " III " IV	30°

ART. XL. — *A New Habit for Chalcopyrite*; by R. W. RICHARDS.

A SPECIMEN of chalcopyrite collected in Somerville, Massachusetts, by Prof. A. E. Dolbear, of Tufts College, some years ago, shows apparently a new and simple habit for the species. The specimen was found in a vein of rusty quartz in the quarry between Broadway and Holland Streets, near Clarendon Hill. The rock of the quarry is the so-called Cambridge or Somerville Slate, referred by some geologists to the Carboniferous, by others to the Lower Cambrian. This rock is a clay-slate cut by many diabase dikes, which in turn are cut by numerous veins carrying a great variety of minerals, among which quartz, calcite, albite, prehnite, babingtonite, erythrite, chlorite and oxides of titanium, recently discovered by Prof. Charles Palache, of Harvard University, may be mentioned.

The crystallization of chalcopyrite is tetragonal, and a sphenoidal habit usually predominates. Prof. S. L. Penfield, in his paper in this Journal on crystals from Chester Co., Pa. (vol. xl, 207, 1890), figured specimens showing prismatic and pyramidal planes, and others showing sphenoid and scalenohedral faces, which he suggests may represent a prism and a second order pyramid distorted by oscillatory combination with the positive sphenoid. The indices he assumes for the distorted forms agree with the forms found on the crystal described in this note.



The Somerville specimen is shown in the cut and possesses only two forms, a prism *m* and a second-order pyramid *e*. These have the indices 110 and 101, respectively, and present the identical faces figured by Prof. Penfield, in a twin crystal (l. c. fig. 8, p. 210). The rough character of the Somerville crystal permitted only contact measurements and the best readings were selected by choice. The angles giving the most satisfactory set of readings are those around the coign *m* to *e*, *e* to *e*, and *e* to *m*. These angles are nearly equal and were found by measurement to be about 60°. This satisfies the relation that should obtain between the planes of the prism and those of the second-order pyramid,

e to *e*, 59° 30·5′
e to *m*, 63° 46·1′.

In Hintze's Handbuch der Mineralogie, sixteen cases are noted of the occurrence of the form *e*, and only seven of *m*. With the exception of one or two cases, either one or the other or both forms are subordinate. The Somerville crystal seems novel in showing these forms predominant and, perhaps, excepting the sphenoid, represents the simplest form of the crystallized mineral.

It is interesting to note that this form differs very slightly from the isometric dodecahedron. This similarity is accounted for by the axial ratio of the mineral, 1 : 0·98525. The resemblance of the crystal to the dodecahedron is well brought out by comparing it with a model of the same. In the drawing and in the crystal itself, the illusion is destroyed by the downward extension of the prism plane.

The crystal is unusually large for the species, having an average diameter of four centimeters. The largest of the Chester County crystals had diameters of a centimeter. Lacroix mentions large crystals from Oued Allelah of Algeria, Africa, having diameters of eight millimeters. The rather indistinct sphenoids from Ellenville, N. Y., have about the same dimensions as the Somerville crystal.

Credit is due to Prof. Palache for assistance in the examination of the specimen and suggestions in regard to its importance.

Tufts College, Massachusetts, 1904.

ART. XLI. — *Molecular Weights of Liquids, with a few Words about Association;* by C. L. SPEYERS.

FOR some years past, evidence has been advanced* to show that

$$\frac{n}{N} = \frac{p-p'}{p'} \qquad (1)$$

agrees with experiment far better than

$$\frac{n}{N} = l\frac{p}{p'} \qquad (2)$$

does. While (1) is as true for concentrated solutions as for dilute ones, (2) fails both in theory and in fact for concentrated solutions, though of course good for dilute ones.

A theoretical foundation was sought for (1) in the notion that a volatile liquid produces those molecules which pass off as vapor *in the body of the liquid* instead of merely on the surface, a notion which J. Traube† is advancing as one of the results of his study of critical phenomena, and that the vapor tension of a liquid is the result of such differentiation in the liquid.

Moreover, on combining (1) with the second law of thermodynamics we get equations for the molecular rise in boiling point and depression in freezing point, for the molecular heat of vaporization and of freezing, and all these independently of the osmotic theory.

Equation (1) has also been advanced tentatively by S. Young and E. C. Fortey‡ but with some reservations in regard to changes in density. The new mixtures that they used were ethyl propionate with ethyl acetate, toluene with ethyl benzene, n hexane with n octane and toluene with benzene. Slight differences were found between observed pressures and those calculated by (1), but no account was taken of a possible association of the vapor of the solvent and so these differences lose something of their significance. In their paper, the writers correct a mistake made by me. They point out that mixtures of non-associated liquids may have minimum boiling points. I stated they could not, and in this respect was wrong, having overlooked the fact that $\Delta p_2/\Delta t$ could be smaller than $\Delta p_1/\Delta t$ at one temperature while greater at another, both temperatures lying within the range of boiling points of the mixtures.

* Journ. Phys. Chem., ii, 347, 362 (1898); Journ. Am. Chem. Soc., xxi, 282 (1899); this Journal, ix, 341 (1900); xiii, 213 (1902).

† Drude's Ann., viii, 267 (1902).

‡ Journ. Lond. Chem. Soc., lxxxiii, 45, 68 (1903).

A word now in regard to association.

Let us consider water. Its density in the gaseous state leads to a formula for its molecule of H_2O. When metals react with it, we get hydroxides and oxides of the general formula $M(OH)_x$ and M_xO_y. In all chemical respects water behaves as if it had the formula H_2O, two replaceable hydrogen atoms and one replaceable oxygen atom, no more, no less. This formula, therefore, has a chemical, a scientific, significance. It states that in chemical reactions two atoms of hydrogen and one of oxygen go together. But in some physical relations, in those relations which involve water as a liquid and in which it stays a liquid, that formula does not account for things. Water is now not so active as corresponds to H_2O. To bring its activity up to what experience has determined to be the normal, the standard, activity, we must take two, three, or more times the mass corresponding to H_2O. We are, therefore, tempted to say water is associated, and to write $(H_2O)_a$ where a runs up to three or four for water and reaches much higher figures with some other liquids. But in so doing we use an unsuitable formula, because the liquid does not behave chemically as this expression suggests. So it is very undesirable to speak of associated molecules. More definite, and far more in accord with what we know, to say that the activity of the water is depressed below the normal than to say its molecule has been associated. The weak notion of associated molecule is replaced by the virile notion of activity. We shall call the above quantity denoted by a, the activity factor. *The activity factor* a *denotes the number of normal grammolecules which must be taken to give an activity equal to the normal, or standard, activity, the standard activity being determined by experience.* We are not to consider a as constant for any liquid but to vary with the conditions as well as with the liquid, and so the objection made by Young and Fortey* that (1) gave values for n which meant $a>1$ in certain mixtures of liquids for which in the pure state $a = 1$ is not valid.

The increased activity beyond the normal, which means $a<1$, called electrolytic dissociation or ionization, is another matter. There are regularities here which enable us to cast the processes into chemical equations. This we cannot do when $a>1$. When $a<1$ we find a chemical activity beyond the normal, so when $a>1$ we may by analogy look for a depressed chemical activity. This idea has not yet been put to the test.

Consider two volatile liquids, 1 and 2, not miscible in all proportions within certain limits of temperature and without chemical action the one upon the other. Let n_1, n_2, denote the

*l. c., 46.

number of grammolecules of each liquid when considered as solute; N_1, N_2, the number of grammolecules of the same liquids when considered as solvent, in computing which the ordinary molecular weight in the vapor state is to be used; p_1, p_2, the vapor tensions of the pure liquids; p_1', p_2', p_1'', p_2'', the vapor tensions of the same liquids in the solutions. Here and elsewhere the two coexisting solutions or phases are distinguished by $'$ and $''$.

At some fixed temperature let us add liquid 1 to a fixed quantity of 2. We have for the two components

$$\frac{n_1'}{N_2'} = \frac{p_2 - p_2'}{p_2'}; \quad \frac{n_2'}{N_1'} = \frac{p_1 - p_1'}{p_1}$$

which hold until the phase disappears entirely. When, on continued addition of 1, a second phase appears, we have the additional two equations

$$\frac{n_1''}{N_2''} = \frac{p_2 - p_2''}{p_2''}; \quad \frac{n_2''}{N_1''} = \frac{p_1 - p_1''}{p_1''}.$$

Since the phases are in equilibrium, $p_2' = p_2''$, $p_1' = p_1''$, and so

$$\frac{n_1'}{N_2'} = \frac{n_1''}{N_2''}; \quad \frac{n_2'}{N_1'} = \frac{n_2''}{N_1''}$$

The proportion of 1 to 2 is different in each phase, wherefore the activity factor, a, for each liquid must be different in each phase. Moreover, the quantity of 1 in 2 being greater in the second phase than in the first, the activity factor, a, is greater in the second phase than in the first, while $a_2' > a_2''$. A jump then in the mutual effects of two liquids, the one upon the other, accompanies the formation of two liquid phases, a jump in the effect of 1 upon 2 being balanced by the jump in the effect of 2 upon 1.

Following custom, we call that temperature above which two liquids dissolve in each other in all proportions, the critical temperature of solution, or for shortness just critical temperature. The composition belonging to the critical temperature we call critical composition and a solution of such composition a critical solution.

Let us start above the critical temperature with a solution of critical composition and with liquid 1 as solute, 2 as solvent, and cool the solution. As we pass down through the critical temperature, the homogeneous liquid separates into two phases, and as the change due to lowering the temperature is continuous, at a temperature infinitesimally below the critical temperature, the compositions of the two phases are only infinitesimally

different, and so their volumes, within an infinitesimal difference, are each one half the original volume, as has been shown by Konowalow.* As we pass on downwards below the critical temperature, the compositions of the two phases diverge, the divergence sometimes increasing indefinitely, sometimes diminishing at lower temperatures with promise of forming later on a homogeneous liquid with a second set of critical quantities.†

Let a_1 be the activity factor of liquid 1, m_1 its normal molecular weight, w_1 its mass in the phase under consideration. Let $t°$ be below the critical value. From 1 we get

$$a_1' = \frac{w_1'}{m_1 N_2'} \cdot \frac{p_2'}{p_2 - p_2'} \text{ and } a_1'' = \frac{w_1''}{m_1 N_2''} \cdot \frac{p_2''}{p_2 - p_2''}. \quad (3)$$

Since two phases are present, w_1' and N_2' as well as p are variable with t and so

$$\frac{da_1'}{dt} = \frac{1}{p_2 - p_2'} \cdot \frac{1}{m_1 N_2'} \left[\frac{w_1'}{p_2 - p_2'} \frac{p_2 dp_2' - p_2' dp_2}{dt} + \frac{p_2'}{N_2'} \frac{N_2' dw_1' - w_1' dN_2'}{dt} \right], \quad (4)$$

where dp_2'/dt is the differential coefficient of the vapor tension of the solution in the immediate neighborhood of the value p_2'; dp_2/dt, that of the pure solvent in the immediate neighborhood of the value p_2. With the exception of

$$\frac{p_2 dp_2' - p_2' dp_2}{dt} \text{ and } \frac{N_2' dw_1' - w_1' dN_2'}{dt}$$

the signs of all the quantities are positive. For dilute solutions we shall put dp_2'/dt from the solution, approximately equal to dp_2'/dt from the pure solvent. That is, we shall assume that dp_2'/dt from the dilute solution is quite close to what we should get were we to differentiate the vapor tension from the pure solvent in the immediate neighborhood of the numerical value p_2'. We do this because we find that in dilute solutions, while the vapor tension curve of the solvent is depressed numerically it is not altered in character, and because we seek the sign of the first quantity rather than its numerical value. With this understanding we find

$$\frac{p_2 dp_2' - p_2' dp_2}{dt} > 0$$

for water, methyl alcohol, i butyl alcohol, amyl alcohol, i amyl alcohol, i butyric acid, carbon disulphide, benzene, and chlorbenzene, and probably for all dilute solutions. Its numerical

* Drude's Ann., x, 360 (1902).
† Ostwald, Lehrb. ii, 670 (1902).

value is not large and does not seem to change rapidly. The other quantity we find is positive when $dw_1'/dt>0$, for then by the nature of the case $dN_2'/dt<0$, and negative when $dw_1'dt<0$ for then $dN_2'/dt>0$. Since $w_1'+w_1''=w_1$ a constant, we have both cases so long as the two coexistant phases are present. For the more dilute phase with respect to 1 $dw_1'/dt>0$, for the more concentrated phase $dw_1''/dt<0$. For this one we write similarly to (4)

$$\frac{da_1''}{dt}=\frac{1}{p_2-p_2''}\cdot\frac{1}{m_1N_2''}\left[\frac{w_1''}{p_2-p_2''}\frac{p_2dp_2''-p_2''dp_2}{dt}+\frac{p_2''}{N_2''}\frac{N_2''dw_1''-w_1''dN_2''}{dt}\right]. \quad (5)$$

From 1,

$$\frac{w_1''}{p_2-p_2''}=m_1\frac{N_2''}{p_2''}$$

which substituted in (5) gives for the bracketed part

$$m_1\frac{N_2''}{p_2''}\left[\frac{p_2dp_2''-p_2''dp_2}{dt}+\left(\frac{p_2''}{N_2''}\right)^2\cdot\frac{1}{m_1}\cdot\frac{N_2''dw_1''-w_1''dN_2''}{dt}\right]$$

The solution now being concentrated, we cannot predict much about the first term from a study of the vapor tension of the pure solvent. I think, however, we may assume that the numerical value of this term will not change rapidly compared with the other term. The second term changes rapidly because it is the arithmetic sum of two quantities, not the difference, and because it has in addition a factor which is the square of a fraction whose numerator and denominator both increase as t increases. Consequently, for quite a wide range in concentration we may look for a negative value for the quantity in brackets and therefore expect

$$\frac{da_1''}{dt}<0 \quad (6)$$

while for the less concentrated solution

$$\frac{da_1'}{dt}>0 \quad (7)$$

At the critical temperature, dw_1'/dt, dw_1''/dt, dN_2'/dt, dN_2''/dt all reduce to zero, and so from (4) and (5),

$$\frac{da_1'}{dt}=\frac{da_1''}{dt}=\frac{da}{dt}=\frac{w_1}{m_1N_2}\cdot\frac{1}{(p_2-p_2')^2}\cdot\frac{p_2dp_2'-p_2'dp_2}{dt}. \quad (8)$$

The solutions being concentrated we cannot predict at all concerning the sign of da/dt from the vapor tension curve according to temperature of the pure solvent, and the data at hand for the vapor tensions of the solutions are limited to a few

cases to be considered after we remark that a set of equations exactly similar to (3), (4), (5), (6), (7) and (8), hold for liquid 2, the two sets of equations being connected by the relations

$$w_1' + m_1 N_1'' = w_1$$
$$w_2'' + m_2 N_2' = w_2.$$

The cases in question are mixtures of anilin with amylene (trimethyl ethylene), and nitrobenzene with methyl iodid, with amylene, with ether, and with pentane, all investigated by Konowalow.* Only the first and last however gave coexistent phases. The others were above their critical temperatures. The highest temperature of the anilin mixture being 25·1° only the amylene was supposed to have an appreciable vapor tension and we are limited to the activity factor of the anilin only. For a similar reason we can find the activity factor of the nitrobenzene only, the temperature of the mixtures containing it being 18·1°.

1

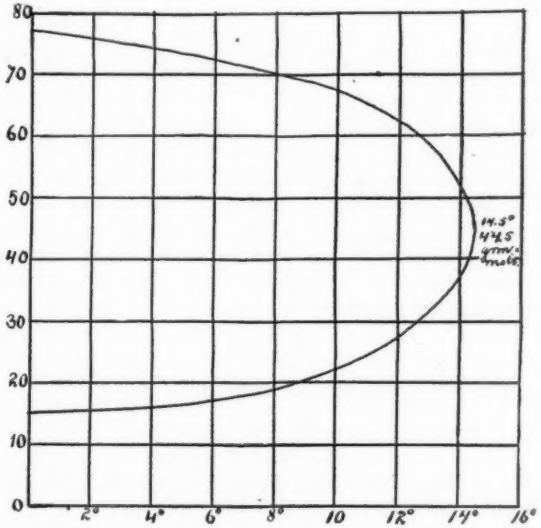


Figure 1 shows the compositions of the two coexistent phases for the anilin mixture from the critical temperature 14·5° down. The critical composition is 44·5 per cent grammolecules of anilin.

The following table contains the data necessary for finding the activity factor of the anilin. In it $t°$ is the temperature, p

* l. c.

the vapor tension of the pure amylene at $t°$, p' the vapor tension of the amylene from the solution, n the per cent grammolecules of anilin in calculating which the normal molecular weight of 93 is used, and a the activity factor computed according to (3) using 70 as the molecular weight of amylene. Should the vapor density of amylene be other than what corresponds to 70, the value for a would have to be correspondingly changed.

$t = 0°$ $p = 180{\cdot}6$mmHg

n	p'	a
10·9	168·9	1·8
[15·0]	164·8	1·8
[77·5]	"	36
81·5	162	38

$t = 14{\cdot}1°$ $p = 331{\cdot}0$mmHg

n	p'	a
7·5	315·0	1·6
20	308·3	3·1
25·3	303·0	3·7
31·1	303·2	4·9
[37·0]		
42·2	301·8	7·5
45·5	302·0	8·7
50·7	302·6	11
[51·0]		
59 8	303·1	16
65·3	301·0	19
75	291·6	22
80	273·0	19

$t = 8{\cdot}1°$ $p = 257{\cdot}8$mmHg

n	p'	a
10.9	241·5	1.8
[19·0]	238·1	2·8
[69·0]	"	27
75	234	29

$t = 18{\cdot}1°$ $p = 391$mmHg

n	p'	a
24·2	354·9	3·1
35·1	352·2	4·9
49	351	8·4
69·9	342·7	16
73·1	336·5	17
82	303·1	16

$t = 25{\cdot}1°$ $p = 498{\cdot}9$mmHg

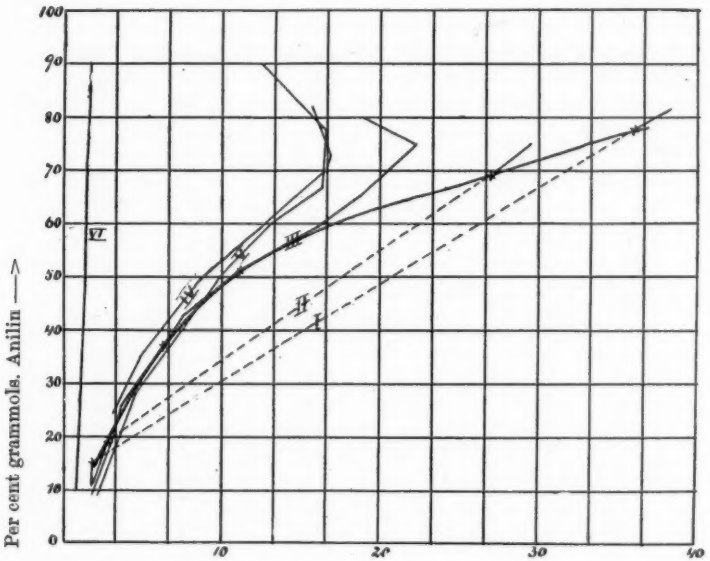
n	p'	a
9.2	476·6	2·2
28·2	458·9	4·5
49·2	453·8	9·7
50·1	453·1	9·9
59·8	447·9	13
66·7	444·2	16
77·7	411·8	16
89·7	295·4	13

From figure 1 we see that at 0° the two layers have the composition of 15·0 and 77·5 per cent grammolecules. These values have been enclosed in [ ], Konowalow giving the vapor tension but not the corresponding compositions. Similarly for the phases at 8·1°. Two phases should have formed at 14·1° but they do not seem to have become visible.

The values for a have been plotted in figure 2. The crosses × mark the compositions of the coexistent phases. Plot 1 corresponds to 0°. We observe that in the phase dilute with respect to anilin, the activity factor is small, only about 2, that is, the anilin is comparatively active, but when the per cent of anilin is large, the activity factor is very large up to about 36 so that now the anilin is very inert. At 0° then we may expect to find dilute solutions of anilin in amylene more active

chemically with respect to the anilin than concentrated ones in amylene. Similarly for plot II at 8·1° and for plot III at 14·1° up to about 75 per cent grammolecules of anilin. From that concentration on and at a temperature around and beyond the critical temperature, the activity factor begins to diminish again, indicating that pure anilin has a greater activity than when in concentrated solutions in amylene.

2



I at 0°, II at 8·1°, III at 14·1°, IV at 18·1°, V at 25·1°.
VI. In $(C_2H_5)_2O$ at 16·2°.

At low concentrations, up to 15 per cent grammolecules of anilin, a increases with the temperature, in accordance with what is stated after equation 4; but at high concentrations, so long as two coexistent phases are present, the reverse is the case, a diminishes as the temperature increases, which is in accordance with what follows after 5. When the temperature rises to 18·1° and the two coexistent phases disappear we find a increasing with the temperature so that in this concentrated solution,

$$\frac{p_2 dp_2' - p_2' dp_2}{dt} > 0$$

just as it would be for pure amylene.

The parabola-like curve shows how a changes with the temperature for pairs of coexistent phases. The dotted lines of I and II connect the coexistent phases. The two ×'s of III are not connected by a dotted line, because the values of the intermediate compositions and pressures are given by Konowalow. He points out that at the temperature to which this curve belongs, which temperature is very close to the critical one, p' varies very slightly with the composition for a range between 25 and 60 per cent grammolecules of anilin, whereas, according to figure 1, this should only be so between the limits of 37 and 51 per cent. We account for this quite readily, by the increasing value of a. Plot VI has been taken from a previous article.*

The following table contains the other data from Konowalow.

Nitrobenzene in methyl iodid.
$t = 18{\cdot}1°$ $p = 310{\cdot}7$mmHg

n	p'	a
19·7	260·5	1·3
40	210·7	1·4
50	185·4	1·5
66·6	137·1	1·6
82	79·5	1·6

Nitrobenzene in ether
$t = 18{\cdot}1°$ $p = 416$mmHg

n	p'	a
16	359	1·2
40·3	294·6	1·6
50·9	261·6	1·8
59·1	232·3	1·8
63·9	215·7	1·9
66·6	203·5	1·9
75	166·3	2·0
76	160·9	2·0
86·6	98·7	2·0
92·5	59·5	2·1

Nitrobenzene in amylene.
$t = 18{\cdot}1°$ $p = 391$mmHg

n	p'	a
16·5	351·2	1·7
32·3	332·9	2·7
41·6	323·7	3·3
59·9	294·8	4·6
66·6	263·8	4·1
78·8	207·9	4·2

Nitrobenzene in pentane.
$t = 18{\cdot}1°$ $p = 536{\cdot}3$mmHg

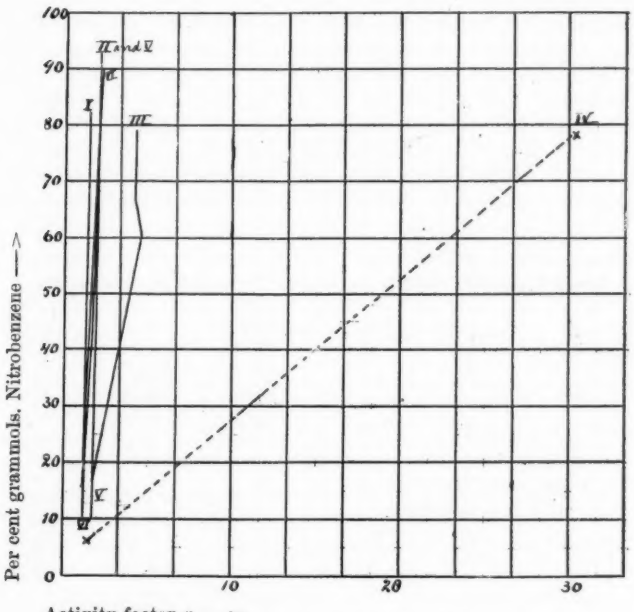
n	p'	a
5·9	514·3	1·5
two layers	504·0	
78·2	479·6	30

These data have been plotted in figure 3. The activity factor of nitrobenzene is pretty constant in methyl iodid and in ether, in amylene it increases considerably as the nitrobenzene increases, while in pentane the increase is 20 times what it was at the beginning. In this case, however, we have two coexistent phases. Unfortunately, the compositions of the coexistent phases are not given, only one composition before the coexistent phases have formed and one after the coexistent

*Journ. Phys. Chem., ii, 347 (1898).

phases have disappeared. The extremities of the broken line of IV mark the compositions of these solutions. I have added plots V and VI taken from an earlier article.* They fit in

3



I. In CH_3I. II. In $(C_2H_5)_2O$. III. In $(CH_3)_2C:CH(CH_3)$.
IV. In C_5H_{12}. $t°=18{\cdot}1°$.
V. In CCl_4 $t°=34.8$. VI. In $(C_2H_5)_2O$ $t=16.2°$.

very well with these of Konowalow and together with VI of figure 2 show how characteristic of two coexistent phases the big jump in the activity factor is.

* l. c.

December 11, 1903.

ART. XLII.—*The Relation of Mass Action and Physical Affinity to Toxicity, with incidental discussion as to how far electrolytic dissociation may be involved;* by J. B. DANDENO.

MASS action, as a principle underlying chemical phenomena, is comparatively well established. The law may be briefly stated, that when any substance in a dissolved state enters into a chemical reaction, the amount of the action is proportional to the active mass of the substance. By mass of substance in solution, or molecular concentration, is meant the number—not actual but relative—of molecules per unit of volume. It may be expressed as so many gram-ions per liter of solution. An illustration of mass action is here given. When potassium nitrate and sulphuric acid are mixed in solution, a reaction, depending upon the mass of each in solution, takes place. Thus, if the acid be in excess, the resulting products are potassium bisulphate ($KHSO_4$) and nitric acid; but if a large excess of nitric acid be added to potassium bisulphate, the resulting products are H_2SO_4 and KNO_3. Such phenomena, though common enough in chemistry, are not well understood.

In this paper an effort is made to set forth one point of view from the physiological side. The radicles of some seedlings are used as the physiological reagent, and a few common solutions as the chemical; and silica to represent a possible physical agent.

By physical affinity is here meant the force of attraction, without chemical change, that substances may have for one another in solution. As will be shown in some of the experiments described in this paper, there is a very considerable amount of such attraction. It has been pointed out* that, with certain toxic solutions, the toxicity was much reduced when non-chemical† substances were present. But just to what extent such non-chemical substances have to do with the well-being of plants, little is at present definitely known. From this it is not to be inferred that such effects are the only effects which may result from the presence of non-chemical substances. It is this action alone,—this hindrance to the chemical action (which would take place if the non-chemical substance were not present)—which is here considered.

The importance of this is at once apparent, when one considers that the great mass of soil particles are non-chemical in their

* Dandeno, Trans. Can. Inst., vii, p. 315.

† By non-chemical substances is here meant those substances which do not react chemically in the experiment in question, and which are not soluble in the liquid used.

nature. The question of fertilizers—one of the most important to the farmer—is essentially a part of this question. For, if the particles of soil can mechanically hold substances in solution, then there will always be a certain amount in the soil which is not available to the roots of the plants. Moreover, roots will be able to withstand a greater amount of poisonous substance in the soil than they could if immersed in a liquid. There are numerous suggestions which may arise along this line, but the discussion in this paper is confined to two phases of the aspect,—(1) that of the inhibitory effects produced by pure sand upon toxic solutions, and (2) that of the relative effects, in the same regard, of fine and of coarse particles.

Considerable has been done within the last eight or ten years towards determining at what concentration of solution certain seedlings will survive, when the radicle is immersed in the solution for a given period of time. Kahlenberg and True,* 1896, record a large number of experiments made with *Lipinus albus*, and deduced certain results, some of which are quite probably unwarranted. Their general method of preparing solutions, a departure from the percentage method, is to be commended, though some confusion in regard to naming of solutions, and other errors of chemical formulæ, make it necessary to be cautious about accepting their results. Heald,† in the same connection, worked with seedlings of *Zea mais*, *Pisum sativum* and *Cucurbita*, but unfortunately confused matters somewhat in the same manner, so that one cannot reconcile his table summarizing results, with the individual tables. For example, on page 152, Heald gives the limit which for corn, just allowed growth as 1/102400 *eq.*, $CuSO_4$; while on page 140, same paper, he records for the same seedling a growth of 16·5 and 7^{mm} (for two successive days) in a solution of $CuSO_4$ 1/102400 *mol.* It seems a pity that more care was not taken in this regard. Stevens‡ worked with spores of a few fungi; and Loew§ gave results of experiments made with seedlings of indian corn.

True and Gies‖ worked with mixed solutions and this work bears somewhat upon the line of thought followed through a part of this paper. True¶ recorded the results of a large number of experiments with *Lupinus albus* along a similar line to that pursued by Kahlenberg and True. True and Hunkel** used certain of the phenols in a similar connection.

Moreover, the same problem has been touched upon from another point of view. O. Loew†† discussed the question of

* Bot. Gaz., xxii, 1896.
† Bot. Gaz., xxii, 1896.
‡ Bot. Gaz., xxvi, 337, 1898.
§ Science, Sept. 4, 1903, p. 304.
‖ Bull. Torr. Bot. Club, xxx, 390, 1903.
¶ This Journal (4), ix, p. 184, 1900.
** Bot. Cent., lxxvi, p. 9.
†† U. S. Dep. Ag., Bull. 18, 1899.

the function of certain of the mineral salts in the soil. Plowman* dealt with the question from the standpoint of electricity and magnetism, using plants growing in flowerpots. He concluded that ionization of the soil bore directly upon growth of plants. Cameron† deals with the same question mainly from the point of view of soils and crops. Clark‡ pursued a line of work similar to that of Stevens.

It is not the intention to give a complete historical bibliography of the subject, but rather to mention some of the more prominent work done directly along this line in order that correlation of data may be available. Due acknowledgment will be made of the work of each in its proper relation to this discussion.

The aim of most of those authors seems to have been to determine, for certain solutions, the concentration at which organs or organisms would just live, or just not live. Nothing apparently is said as to whether quantity of solution had anything to do with the life of the organism. Nor is anything said of the question as to whether the shape of the vessel, or the presence of foreign non-chemical bodies might have any influence upon the action of the substance in solution. The quantity of solution used was apparently considered of little importance by some of those who made experiments along this line, for little or no mention is made of quantity. Cameron (Bull. 71) and Loew (l. c.), however, are clear on this point.

The method of preparing solutions was in strict accord with the plan of chemical equivalents, that is to say, the solutions were so prepared and named that n stands for a gram-equivalent per liter of solution in each and every case. The number in the denominator of the fraction whose numerator is n, denotes the concentration of the solution under consideration. Where the acids or salts are monobasic, the gram-molecule is the same as the gram-equivalent; where the acid or salt is dibasic, then one-half the molecular weight to a liter is the gram-equivalent. It is not necessary to mention acids or salts of other basicity, as the two mentioned are the only kinds used in the experiments here described. In the case of the so-called acid salt ($NaHCO_3$), one-half the molecular weight in grams dissolved to a liter is the gram-equivalent per liter solution,—exactly similar in concentration to that of the carbonate (Na_2CO_3). This may seem unduly explicit on this

* This Journal (4), xiv, p. 129, Aug., 1902.

† (*a*) U. S. Dep. Ag., Bur. of Soils, Bull. 22, 1903.

(*b*) Jour. Phys. Chem., viii, 1, Jan., 1904.

(*c*) Bull. 71, U. S. Dep. Ag. This contains a particularly valuable discussion of the matter, Kearney being associated with Cameron in the work.

‡ Bot. Gaz., xxviii, p. 409.

point, but it is necessary to be so, considering some work which has been done along a similar line. For example, True* states, referring to H_2SO_4: "And since it splits off two H ions from every molecule, it would have in chemically equivalent quantities twice the number of H ions found in HCl." The author just referred to evidently had an erroneous view as to what chemical equivalent quantities meant, although he had previous to this published some papers (one of which has already been referred to) on a similar character of work. Hence it may be seen that care, both in preparing and in naming solutions, is very desirable.

The solutions used in the following experiments were selected because they represent the chief types,—acid, base, and toxic salt. The carbonate and the bicarbonate were used in order to see how physiological reactions might harmonize with the theory of electrolytic dissociation. Carbonic acid presented a peculiar aspect of the question, inasmuch as it is an acid which is said to dissociate, and yet it produces almost no toxic effect at the highest concentration obtainable.

The method of marking and of measuring the radicles, and the test applied to decide the question of death, were according to the method of Loew[6], namely, that of a growth in water after having been submitted to the solution test. If growth took place in the solution, and then in water, the radicle was considered living; but if no growth took place in water—after the twenty-four hours in the solution—the radicle was considered dead. For measuring the growth of the pea and the corn, a mark was made on the glass vial on one or both sides; then sighting through in line with the root tip, measurement could thus be made very accurately, and certainly very conveniently. In the case of the lupine, a mark was made with india ink at, or a little below, the junction between the root and stem; and this mark kept above the solution. Measurement was made from this mark to the end of the root tip and recorded.

An attempt was made to follow the method of marking adopted by Heald, and Kahlenberg and True, but it was found too clumsy for the purpose, mainly for the reason that the india ink would "run" so as to leave the mark upon the root broad and indefinite, and in some cases the mark was entirely lost when the portion of the radicle on which the mark was made was in the solution.

The seedlings used were *Zea mais* (common field corn, yellow dent variety), *Pisum sativum* (small field pea) and *Lupinus albus* (white lupine). These were selected chiefly because they were convenient for the purpose; and also because other inves-

* This Journal, vol. ix, March, 1900, p. 184.

tigators had worked with the same kind of seedlings, rendering comparison of results possible. Seedlings were prepared in the usual way, and were used when the radicle was of a suitable length. However, none was used whose radicle was less than 12^{mm} in length.

For the test in regard to physical affinity, a pure sand was obtained from ground quartz. This was thoroughly washed, first in strong HCl, then in water, and lastly in distilled water several times. Two grades were secured, *fine* and *coarse*. The particles of the fine sand were of such a size that the volume of one grain was $\cdot0655^{cbmm}$, and a grain of the coarse sand $\cdot22^{cbmm}$. The surface area of the fine sand is to the surface area of the coarse sand, therefore, as 3 : 2, in a given mass of sand. From this it is not to be inferred that all the grains were exactly of the same size. The measurements given are an approximation towards an average. A further test was made to see how great the volume of air space would be in the one as compared with that of the other. The following was the result of careful experiments: In a total volume of $15\cdot6^{cc}$, there was, in the case of the fine sand, $5\cdot6^{cc}$ of air and 10^{cc} of sand. Of the coarse sand, in a volume of $15\cdot6^{cc}$, there were $6\cdot0^{cc}$ of air. Both were tested as nearly as possible under the same conditions of packing. Several tests gave the same result. It thus appears that the coarse sand contained a little more air space than did the fine,—actually 38·4 as against 35·9 per cent, in proportion to total mass of sand and water.

The volume of sand used per seedling was 12^{cc}, and 8^{cc}, in the case of both kinds of sand. As no difference was observed in regard to growth whether the quantity was 12^{cc} or 8^{cc}, no mention is made in the records.

Some of the experiments seemed to show that the shape of the vessel in which liquid tests were made had a perceptible influence upon the power of the seedling to resist the toxic action of the solution, resulting possibly from inequality of diffusion. But in all tests recorded in this paper, the vessels were homeopathic vials of uniform proportions for all the sizes (from 25^{cc} to 1^{cc} capacity).

For corroborative tests, the seedlings were germinated in calcium chloride tubes, the "seed" remaining in the bulb and the radicle growing down through the small end. Manipulation was thus very convenient, and the minimum of damage done the seedling in the process of transfer and of marking. This test was made only with seedlings whose radicles had penetrated *beyond the end of the tube.*

The different tests used by the various investigators to decide death renders it extremely difficult to make comparisons. The

test here, as has already been stated, is the capability of making further growth. In nice distinctions the mere appearance is not a sufficient test; but strange as it may seem, this has been the most general criterion. However, in the most critical point this test fails. Jones (Theory of Elect. Chem., p. 269) states: "It was a simple matter to determine when the root was dead, since it lost its satiny lustre and acquired a dead white color." This is just what it is almost impossible to do. Cameron* gives it as a test of death that when the first 15^{mm} became flaccid, death resulted. From this it may be inferred that, if the radicle became flaccid the first 13^{mm}, or the first 10^{mm}, or even the first 5^{mm}, the seedling would be recorded as *living* in that solution. Where the radicles did not become flaccid at death he does not say how he decided the matter. He contents himself with saying that it required *much experience* and *nice judgment.*

Vagueness is occasional even in measuring. Kearney and Cameron (l. c.) state: "The radicle had somewhat elongated from the plumule to the apex." They may mean from the terminal bud to the apex of the root; or, possibly from one end of the radicle to the other, two very different things.

The tables contained in this paper (unless otherwise stated) are records of *average* experiments of each type. It would occupy far too much space to give all the records, because a large number of experiments were made in each class, often as many as twenty seedlings being submitted to the test. Experiments were frequently repeated, sometimes out of mere curiosity, but all the evidence obtainable was used to strengthen whatever results are here set forth. One or two seedlings, in a test of this nature, is not enough. Occasionally a seedling will die, even in water, and it is extremely difficult to tell why.

To show an example of the comparisons of growth made in regard to quantity of solution used, one experiment is here below recorded.

I.

PEA, HCl $n/2048$.

Quantity of solution.	Growth in 24 hours in solution.	In water, growth in 24 hours.
25^{cc}	0^{mm}	0^{mm}
20	0	0
12	0	0
8	0	0
5	3	0
$2\frac{1}{2}$	12	11
1	12	16

Such experiments as the one whose results are just given form the basis for the figures in Tables II–IX.

* Journal Phys. Chem. xiii, 3, 1904.

The columns in the following tables (I–IX), under concentration used, are divided into four parts, and these are subdivided,—A, B, C, D. In the column A is given the number of cubic centimeters in which the radicles plainly lived and grew. In B is given the number of cc. in which the radicles died. Column C contains the average number of mm. the radicles grew during twenty-four hours' immersion in the solution used. This number is not the maximum average, that is to say, it is not a measure of the growth which might be obtained in a quantity of solution much less than the one given in column A. In column D is recorded the average growth obtained in twenty-four hours when the radicle was in water, after having been taken from the solution. This also refers to the seedlings grown in a quantity as indicated in A.

II. H_2SO_4.

	n/1024				*n*/2048				*n*/4096				*n*/8192			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
Pea					2½	5	5	5	5	8	7	4	12	25	3	0
Lupine					5	8	5	7	12	20	2	6	25		7	9
Corn	1	2½	5	14	12	20	5	10	20	25	5	2				

III. HCl.

	n/1024				*n*/2048				*n*/4096				*n*/8192			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
Pea					2½	5	12	13	5	8	8	4	12	20	8	2
Lupine					2½	5	12	22	5	8	3	8	20	25	8	3
Corn	1	2½	8	10	2½	5	12	10	12	20	6	3	25		13	3

IV. H_2CO_3.*

	n/171				*n*/343				*n*/513			
	A	B	C	D	A	B	C	D	A	B	C	D
Pea					20	25	11	12	25		12	15
Lupine	25		7	3								
Corn	25		16	35								

V. $CuSO_4$.

	n/32768				*n*/65536				*n*/131072				*n*/262144			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
Pea	2½	5	16	0	8	12	18	0	12	20	4	0	25		10	6
Lupine	5	12	4	6	25		7	30								
Corn									1	2½	3	13	20	25	7	8

* This is considered a divalent acid, though Cameron regards it as a monovalent acid (HCO_3).

VI. KOH.

	n/64				*n*/128				*n*/256				*n*/512			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
Pea									4	8	11	4	25		15	12
Lupine					4	8	11	8	25		12	13				
Corn	1	2½	6	4	25		13	11								

VII. NaOH.

	n/64				*n*/128				*n*/256							
	A	B	C	D	A	B	C	D	A	B	C	D				
Pea					3	8	7	8	25		8	12				
Lupine	1	2½	3	10	25		9	6	25		12	10				
Corn	2½	5	12	15	25		19	16	25		16	12				

VIII. Na_2CO_3.

	n/32				*n*/64				*n*/128				*n*/256			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
Pea													12	25	10	7
Lupine									8	20	10	5	25		8	9
Corn					12	20	10	5	20	25	8	3	25		6	4

IX. $NaHCO_3$.

	n/8				*n*/16				*n*/32				*n*/64			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
Pea					3	8	3	2	8	12	7	11	12	20	3	6
Lupine					20	25	4	5	25		5	6	25		13	35
Corn	1	2½	3	8	25		7	6	25		9	20	25		12	42

During the course of many of the experiments made with radicles immersed in solution, certain phenomena seemed to indicate that the action which took place between the substance in solution and the radicle was chemical in its nature. Consequently, experiments were made to ascertain, if possible, how much reaction the radicle might produce if allowed to react upon the solution for a given time. Two of these experiments are here recorded, one of them employing HCl,*n*/1024 and the other H_2SO_4,*n*/1024. In both cases corn seedlings were used. In column 1 is given the volume of solution used in each case; in column 2 is given the growth in millimeters of the radicles during twenty-four hours; then these seedlings

were taken from the solution and fresh seedlings put in their places in the same solution. In column 3 is recorded the growth of seedlings during one day,—the second day the seedlings were used. These were, of course, the same solutions which had been used the previous day. This was continued for eight days. In column 6 is the recorded growth for two days. In all other cases the growth is for a period of twenty-four hours. The same solutions, therefore, were employed for eight days, and seven series of fresh seedlings were used in the test.

X. Corn, HCl, *n*/1024.

1. Quantity of solution.	Growth at the end of,—						
	2	3	4	5	6	7	8
	1 dy	2 dy	3 dy	4 dy	6 dy	7 dy	8 dy
25cc	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0
12	0	0	0	17	12	8	23
8	0	0	0	14	20	13	28
5	0	8	3	9	10	*	*
2½	0	8	20	22	18	*	*
1	8	10	2	24	*	*	*

XI. Corn, H_2SO_4, *n*/1024.

1. Quantity of solution.	Growth at the end of,—						
	2	3	4	5	6	7	8
	1 dy	2 dy	3 dy	4 dy	6 dy	7 dy	8 dy
25cc	0	0	0	0	0	0	0
20	0	0	0	0	8	5	10
12	0	0	0	6	6	8	25
8	0	0	10	24	16	7	24
5	0	14	15	22	8	*	*
2½	0	12	30	22	20	*	*
1	5	14	13	20	*	*	*

From these tables it seems reasonably clear that *quantity* of solution bears certain relations to toxic action. In Table I is shown a sort of limit in quantity, somewhere between 2½ and 5cc, the seedlings plainly living in quantities of 1 and of 2½cc; while they just as plainly died in quantities ranging from 5cc up through 25cc. The action is probably a chemical one, resulting from the substances supplied to the solution by the plant; or, it may possibly be a physical action produced upon the solution by merely extracting certain substances mechanically from the solution. It is by no means easy to decide which

* No tests were made, as growth was quite evident.

it may be. In each case the toxic action of the solution is reduced; in the former by neutralization and in the latter by extraction of the harmful element. This is plainly shown in Tables X and XI. Each seedling makes the solution less toxic, as is shown from the fact that on the first day the seedlings lived in a quantity of 1^{cc} in the case of both acids, while on the eighth day they lived in a quantity of 12^{cc}.

Larger quantities than 25^{cc} were used, but no difference was noticed. In fact, when two or three seedlings were placed in a beaker (100^{cc}) with radicles immersed, it usually happened that they stood the concentration better than when placed singly in vials containing only 25^{cc} of solution.

Small quantities, as a rule, gave the most clear-cut reactions, probably because of the fact that diffusion in solutions is so very slow, making it possible for a considerable quantity of the solute or of the ions to lie in a part of the solution too far from the radicle of the seedling, to affect it. But in the case of small quantities, diffusion will enter into the problem to no very great extent, rendering it possible to obtain results which are more nearly accurate from a chemical point of view.

The actual amount of toxic ions overcome in 24 hours by a seedling of corn with H_2SO_4 and HCl is 1^{cc} of $n/1024$, giving a result of $1/000 \times 1/1024 = 1/1024000$ grams of ionic hydrogen. This may be expressed in another way:—1,024,000 seedlings would resist the toxic action produced by one gram of ionic hydrogen. It may be proved absolutely, as indicated in Table II, column A, of a concentration of $n/1024$. For, if a gram-equivalent solution be diluted to $n/1024$ and divided up into quantities of 1^{cc}, and a seedling be placed in each, they would all grow; but if divided up into quantities of $2\frac{1}{2}$^{cc}, and a seedling placed in each, they would all die. For more dilute solutions, the seedling can live in the presence of a far greater amount of ionic hydrogen, showing that diffusion is remarkably slow and that the action of the mass of the water is considerable. The number of gram-ions in a solution $n/2048$ would be half as many per unit of volume; but the corn seedling lives when submitted to 12^{cc} of this solution. It ought, however, to withstand only 2^{cc}, if diffusion were perfect and mass action eliminated. Consequently, the injurious ions in 10^{cc} of the 12^{cc} used are prevented from acting upon the radicle from the fact that the mass of liquid is great enough to render $10/2 \times 1/102400$ grams of ionic hydrogen harmless, when in a quantity of 12^{cc}. This is the condition of affairs with corn for H_2SO_4. It is apparently different with HCl at the dilution mentioned but similar at the next lower dilution. Where the seedling is particularly sensitive to the solution, as with the pea, there is small difference in relatively great concentra-

tions, the difference being greater and greater as the amount of solution increases. So that beyond a certain limit of concentration, no matter how much ionic hydrogen be present, this hydrogen is prevented from acting on the radicle by the mere presence of the mass of water. This is probably because diffusion is so very slow. The corn seedling theoretically should resist 1, 2, 4, 8^{cc} of HCl in the 4 dilutions given in Table III, if diffusion were perfect. But it does actually resist 1, 2½, 12, inf., Table III, so that the difference in quantity due to mass action is represented by the differences between the pairs of numbers in the series thus,—0, ½, 8, inf. Now, in $n/8192$ the lupine or the corn will counteract the harmful ions as fast as they come in contact with the radicle, so that the dilution at which the seedling lived in 25^{cc} may be said to be the dilution where diffusion and vital activity are balanced. The limit of resistance, therefore, for corn is 1^{cc} of $n/1022$; and of 25^{cc} $n/8192$.

It has been pointed out (3, l. c. p. 90) that lateral roots which develop after a seedling is placed in a test solution may live and grow even though the radicle itself be killed. Kahlenberg and True suggest that this is due to a power of accommodation, but this is quite probably not so, because in a number of experiments with seedlings which had withstood one solution, an attempt was made to have them grow in a solution a grade stronger, or in the same solution in greater quantity, but without success. Seedlings showed no power of accommodation. It is more probably due to the fact that the radicle has already partly neutralized the solution, as appears in Tables X and XI.

The strongest solution of carbonic acid (H_2CO_3) which it was possible to obtain was $n/171$ by actual titration test. Seedlings of corn and lupine stood this concentration readily, but the pea did not. With the largest quantity of solution used (25^{cc}) the pea survived in $n/513$ but died in $n/342$.

H_2CO_3, according to the theory of dissociation, may dissociate into H ions and CO_3 ions, or possibly into H ions and HCO_3 ions, more probably the latter, reasoning from such data as we have concerning $NaHCO_3$. Neither case can be true, speaking in the language of the theory of electrolytic dissociation, because, if there were H ions present in such quantity as is indicated by a dissociation into H ions and CO_3 ions, then it would be as toxic as H_2SO_4, but, from those experiments, it can scarcely be one-fiftieth as toxic. The other alternative method of dissociation can not account for this either, for a similar reason. These results are in opposition to the theory of dissociation.

The experiments with sodic carbonate show that the corn seedling endures a solution of $n/128$ in 25^{cc}. From the side of the theory of dissociation this substance should permit

growth at about $n/16$, because sodic chloride, which is about 5/6 dissociated at this concentration, permits growth. The sodium, in the case of NaCl, appears to be but slightly toxic. Nor can the CO_3 ion be very toxic, from Table IV. Whence then this great toxic action of Na_2CO_3? Basing our views upon the theory of electrolytic dissociation, it ought to be about the same as NaCl or Na_2SO_4. But it is far more so. From this it would seem that the theory was insufficient, or possibly erroneous. The explanation, in the writer's opinion, is that the Na_2CO_3 breaks up, in aqueous solutions, into Na_2O and CO_2 and then reacts thus:—$Na_2CO_3 + H_2O = 2NaOH + CO_2$. It would then be practically a solution of NaOH of a concentration identical with that of Na_2CO_3, which was chemically equivalent. This is quite probable from these experiments. If this explanation be correct, the theory of dissociation may give very misleading notions as to the actual condition of affairs.

The bicarbonate of soda affords another illustration. This may dissociate into Na and HCO_3, or into H and $NaCO_3$, or into Na, H, and CO_3. The experiments show that the pea will grow in 25^{cc} $n/128$ and in NaOH $n/256$. If the bicarbonate dissociate according to the first plan, the seedling ought to live in a solution about $n/8$; and if according to either of the latter, in a solution of about $n/2048$. It, however, does neither.

Pea seedlings will live in small quantities of the bicarbonate at a strength of $n/16$ and in similar quantities of NaOH at $n/128$, but in chemically equivalent quantities there is just half as much sodium in the bicarbonate as in the hydroxide. They would compare then at about 4:1 in toxicity, the hydroxide being the stronger. But since this substance may dissociate in three ways at least, we may have a dissociation as follows, with possibly an accompanying chemical action; $8NaHCO_3$ produces $Na_2O + 2CO_2 + H_2O$ and 6Na and $6HCO_3$. This might easily give a chemical reaction from Na_2O and H_2O of 2NaOH. Hence from 8 molecules we get 2 molecules of NaOH or 2 OH ions. The ions Na_3 and HCO_3 are probably harmless, judging from Table IV. This is in the language of the theory. These explanations throw some light upon the alkaline reaction on litmus, and other indicators, of the so-called acid salt $NaHCO_3$. Theoretically it ought to react acid, if anything, but practically it reacts rather strongly alkaline.

Similarly also with Na_2CO_3. Theoretically it ought to be neutral, but it actually reacts very strongly alkaline. The explanation, therefore, is, that in the process of dissolving in water, an actual chemical reaction takes place by some rearrangement of the molecules, or groups of molecules, in the solution. The ionization theory does not aid at all, rather the

reverse. Ionization *may* take place, but a further reaction must be assumed in order to account for the phenomena referred to, both chemical and physiological.

In order to test the effects of a foreign body upon the solute, pure clean sand (silica) was mixed with the solution, and the radicle immersed in the mixture. The vials were of similar proportions to those used in the liquid tests. The actual net volume of the sand employed was from 5 to 8^{cc}, and of liquid $3\frac{1}{2}^{cc}$ to 6^{cc}. Each seedling was exposed two days to the mixture, and afterwards tested for further growth in water. One reason for exposing two days instead of one—which was done with the liquid tests—was to make absolutely certain that whatever deductions in regard to power to resist the toxic reagent, should be on the safe side, because some seedlings can endure a solution for one day when they could not for two days.

In column A, under the given concentration, is placed the average number of mm. the radicle grew in length during forty-eight hours; and in column B the average number of mm. the same seedling grew when immersed in water after being removed from the mixture (solution with sand). In one respect, therefore, the test was a severer one than when the seedlings were immersed in the liquid, because they were exposed to the reagent twice as long.

II.a, H_2SO_4.

	n/256		*n*/512		*n*/1024	
	A	B	A	B	A	B
Pea	0	0	14	8	6	10
Lupine	0	0	13	10	13	3
Corn	3	0	22	29	25	15

III.a, HCl.

	n/512		*n*/1024	
	A	B	A	B
Pea	6	2	27	10
Lupine	4	5	24	6
Corn	29	17	35	15

IV.a, H_2CO_3.

	n/171	
	A	B
Pea	8	9

V.a, $CuSO_4$.

	n/2048		*n*/4096		*n*/8192		*n*/16484	
	A	B	A	B	A	B	A	B
Pea	2	0	4	3	4	7	28	17
Lupine	7	0	5	6	10	3	13	14
Corn	2	0	16	5	23	10	3	4

VI.a, KOH.

	n/32		*n*/64		*n*/128	
	A	B	A	B	A	B
Pea	0	0	3	0	10	12
Lupine	0	0	4	0	11	5
Corn	0	0	12	10		

VII.a, NaOH.

	n/32		*n*/64		*n*/128	
	A	B	A	B	A	B
Pea	0	0	1	0	18	16
Lupine	0	0	0	0	6	4
Corn	0	0	11	10	17	11

VIII.a, Na_2CO_3.

	n/8		*n*/16		*n*/32	
	A	B	A	B	A	B
Pea	0	0	0	0	8	5
Lupine	0	0	2	0	9	7
Corn	0	0	5	0	28	11

IX.a, $NaHCO_3$.

	n/4		*n*/8		*n*/16	
	A	B	A	B	A	B
Pea	0	0	0	0	8	9
Lupine	0	0	3	0	6	7
Corn	0	0	15	11	2	2

A comparison of data taken from Tables II–IX (those in which radicles were immersed in liquid) with those taken from Tables IIa–IXa (those where radicles were immersed in sand and liquid) may help towards a clearer notion of the action produced by a non-chemical body. In making comparisons, the actual mass of solution used was arranged so as to have, as nearly as possible, the same in each case, with a view towards eliminating every element of inequality excepting the one under consideration. It proved, however, that a difference in quantity, ranging from $3\frac{1}{2}^{cc}$ to 6^{cc}, of actual liquid used, when mixed with sand, produced no noticeable difference in action upon the radicles.

In solutions of HCl and H_2SO_4, *n*/512, all seedlings mentioned, live with at least 3^{cc} of liquid, when sand is present; but in liquid alone, similar seedlings, under similar circumstances, can scarcely endure a concentration of *n*/2048, or in a ratio of 4 : 1. This shows that the actual physical effect of the sand was equivalent to a neutralizing reaction of $9/2048^{cc}$ normal acid in 1^{cc} of solution, because the seedling lived in a solution $3/512^{cc}$, or 12/2048 of normal acid to 1^{cc} of solu-

tion. When in liquid alone, radicles withstand barely 3^{cc} of $n/2048$* solution, or $3/2048^{cc}$ per 1^{cc} of normal acid; therefore 9/2048 represents the physical effect of the sand with the two substances used. This is about 4:1, at or near the limit where root tips just resist the acid and live.

Similarly for KOH and NaOH, with the pea and the lupine, the sand retards the action of 3/256 of 1^{cc} of normal KOH near the resisting limit. For KOH and corn it is 3/128 of 1^{cc} normal.

The seedlings withstood relatively a very great concentration of $CuSO_4$ when sand was present; actually $n/4096$ (Table Va) as against not less than $n/32768$ without sand. This seems to be due again to the presence of the non-chemical body. The reason why the toxic action is so much reduced with this substance is probably because, as has already been mentioned, the attractive force of the sand is constant, and requires satisfaction; therefore, in dilute solutions, where there is so much less of the solute per unit of volume, the seedling would be relieved of a large proportion of the harmful element. The actual amount for this solute would be $3/4096 - 3/32768 = 21/32768$ gram-ions of copper. This hindrance to toxic effect of the solute is probably also due in some measure to the retarding effect upon diffusion caused by the presence of the foreign body.

The suggestion which arises from this non-chemical action of sand is that soils may hold mechanically a portion of a solute, and may never give it up. It may be forced to liberate a part of it by the application of another solute which might, in part, satisfy the attractive force exerted by the particles of soil. This may also account for the fact that a chemical analysis is not always a final argument as to the fertility of soil. For instance, suppose KNO_3 were applied in a certain quantity to a pure sand, and plants be allowed to grow for a time in this, it would be found that the plants had been unable to extract all the KNO_3; but if another substance, say $Ca(NO_3)_2$, be then applied, the amount of KNO_3 available might be increased, though no chemical action take place. It is probably thus with the whole subject of fertilizers. A substance may often liberate an important element by taking its place mechanically in the soil, though the substance which had been applied have itself no fertilizing value. The writer is aware that many consider a chemical analysis of soil a definite basis for a liquid nutrient solution, and *vice versa*. Cameron. (Bul. 22, U. S. Dep. Ag., p. 15), quoting Johnson, states: "The analysis of the well water shows that a nutritive solution need not contain

* Slight exceptions to this may be noticed as shown in Table II, but calculations are made only from the most certain limits.

the food of plants in greater proportion than occurs in the aqueous extract of ordinary soil." This is probably the reverse of the actual condition, because, as has already been pointed out, the soil particles have a physical attraction to be satisfied.

The question of selective power of plants is a vague one. It is probably more a name than a fact. The soil selects as well as the plant.

So far as this physiological problem is concerned, it seems that the theory of electrolytic dissociation is insufficient. Certainly no support to the theory comes from the physiological side. Acetic acid, sodic carbonate, sodic bicarbonate and carbonic acid exhibit phenomena quite in opposition to it. Conclusions have been published which, from the data, seem to be entirely unwarranted. Cameron virtually points this out, saying: "The necessity of such assumption would seem to absolutely invalidate the use of such organisms and criteria for the testing of the dissociation hypothesis in any quantitative way." On the other hand, in Jones' 'Theory of Electrical Dissociation,' p. 272, is stated: "The theory of electrolytic dissociation has thus thrown light upon the physiological action of different substances, and the theory has itself been strengthened by these experiments upon living things." Now the experiments recorded in this paper show that the theory throws no light upon such physiological problems, rather the reverse, if anything. A further quotation will show that Jones did not examine the matter as carefully as might be expected, in consideration of the fact that he was compiling a text-book. He states, p. 271, referring to the work done by Heald: The Cu ion is about as toxic as the hydrogen ion," and on page 270: "In the case of strong acids the root would just live in a solution which contained a gram molecular weight of the acid in 6400 liters," and further on: "The roots would just survive in a solution which contained a gram molecular weight of copper ions in 51200 liters." It should be remembered that these quotations from Jones are taken from a recent text-book. A glance at them will convince one that little, if any, care has been taken to present the matter accurately. This is a misinterpretation of Heald for which Heald is in no way responsible.

In the first place, there is no evidence from the physiological side for the theory of electrolytic dissociation, and in the second place, references have been made over and over again to the earlier investigations, with no sure foundation. When these creep into text-books, it is supposed they are considered to be established facts, and, therefore, all the more need to call attention to them.

An illustration may show the mistaken notion following the application of the theory of dissociation to explain certain

physiological phenomena. Heald (l. c., p. 136) states: "Now the carbonic acid in aqueous solutions will dissociate to form H ions and CO_3 ions." This is of course quite probably not correct. He states further, p. 137: "More experiments are necessary to prove conclusively the fact that CO_2 poisoning is due to the effect of the ionic H, and as soon as possible experiments with that view will be carried out." From this latter quotation it is quite clear the author had no experimental evidence in regard to H_2CO_3, yet in the same connection he asserts it as a fact that it dissociates into H ions and CO_3 ions. If the toxic action be due to the H ions,—assuming his prediction of the substance to be warranted—it should be as toxic as H_2SO_4. But it is only about one-fiftieth as toxic as H_2SO_4. This is an illustration of prediction based on the theory of dissociation without basis in fact. The author just referred to is not alone in this respect; and the whole tendency, the whole spirit of the paper, as well as those of some others, seems to *assume the theory of electrolytic dissociation is true, and see if physiological action fits in;* and where it does not, as in acetic acid, *make it fit by assigning function to the whole molecule.*

A cursory glance at the situation might lead one to suppose that the apparent uniformity of toxic action of certain substances, e. g., HCl and H_2SO_4, did show a sort of harmony with dissociation. However, a careful examination of this reveals the fact that it is quite to be expected that these substances would act thus, for the simple reason that they are *chemically equivalent* as a basis of operation. It is not to be wondered at, therefore, that there is such harmony. It could scarcely be otherwise: and so on along the whole line, whether dissociation occurs or not. The only fair conclusion seems to be that the toxic action is a chemical action, because all concentrations made use of are *chemical equivalents.* Jones, p. 268, states: "It had been thought that the physiological action of any substance was due to its chemical nature." Kahlenberg and True, p. 85, state: "It has always been taken as axiomatic that the physiological action of any substance is due to its chemical character." Notwithstanding these statements, from the experiments recorded in this paper, *it should be still so considered.* There seems no doubt whatever that the physiological action is due to the chemical properties of the solute. Though the writers just mentioned do not attempt to explain what the nature of the action may be, they lead one to infer that it is due to some subtle action of a physical nature, involving, it may be, a charge of electricity with which the ion is thought to be loaded.

Dissociation under ordinary circumstances may not take

place at all. The only reliable test to the matter is the conduction of electricity. But this very test may actually *bring about* dissociation, instead of merely showing that it already exists in the solution. Moreover, the theory of the cause of osmotic action does not throw light upon the matter, as notice the results of Morse and Frazer* on sugar solution—a non-electrolyte. They obtain a pressure of about 32 atmospheres, where, according to the theory of dissociation, it ought to be but 22·6. The high vapor densities of certain substances and the lowering of the freezing point of solutions may be explained on other grounds upon which it is not necessary to enter here.

The toxicity of compound ions,—those which are composed of more than one element,—has been discussed by Clark and by Kahlenberg and True, but with diverse results. Clark concluded somewhat generally that a compound ion was *more* toxic than a simple ion. The experiments of Kahlenberg and True lead one to the conclusion that the compound ion is much *less* toxic. They state, referring to such compounds as H_3PO_4, that the acid dissociates into H and H_2PO_4, and the acid H_3PO_4 is equally toxic with HCl. This shows that they consider the H_2PO_4 ion as practically non-toxic, or slightly so. They state further, referring to potassium silver cyanide, that the complex ion $Ag(CN)_2$ is far less poisonous than the Ag ion alone. They say also that ferric ions are much more poisonous than are the complex ions containing ferric iron. Clark, on the other hand, reasoning also apparently from the theory of dissociation, referring to H_2SO_4 states that the ion HSO_4 is 1·3 times as toxic as H, and that the whole molecule (HNO_3) is 7 or 8 times as toxic as the simple ion H.

No attempt is here made to reconcile these statements, for it is impossible to do so. But it shows quite clearly that it is also impossible to reconcile the theory of dissociation with experimental evidence. It shows further, that one can not predict just what will be the physiological result if the basis for prediction be laid upon the theory of dissociation.

Another illustration of the danger in attempting to harmonize the theory of dissociation with physiological phenomena, is furnished by a comparison of toxic action between Na_2SO_4 and NaCl. Cameron places the toxic limit of the former at $3n/400$, and True places that of NaCl at $n/16$.† Now, according to the theory of dissociation (as discussed by Kahlenberg and True), there appears a contradiction; for, since the anion is a negligible quantity in each case, the kation must account for the difference, but the kations are identical. The difference above noted is also too large to be a mere personal difference. Assum-

* Science, ii, 16, 883.

† Cameron gives the limit for NaCl at $n/50$, which is probably correct.

ing Cameron's figures, there is still a wide difference between these two salts with a common kation. But it might be argued that the anion may cause the difference. Let us assume it does. Then, in the case of H_2SO_4 and HCl we have a common kation again, with each of the two anions before mentioned. A comparison of these ought to show H_2SO_4 more toxic than HCl. But all experiments prove rather the reverse. HCl is slightly more toxic (see Tables X, XI, I, II.) Even assuming Kahlenberg and True's own figures for these substances, we find no greater toxic action for H_2SO_4. Considering the comparison between NaCl and Na_2SO_4 we should expect to find it decidedly more toxic.

XX.

		Liquid test.			Liquid and Sand test.
1	2	3	4	5	6
H_2SO_4	pea	2048	2½	16382	512
"	lupine	2048	5	8192	512
"	corn	1024	1	8192	512
HCl	pea	2048	2½	16384	512
"	lupine	2048	2½	16384	512
"	corn	1024	1	8192	512
H_2CO_3	pea	343	20	513	171*
$CuSO_4$	pea	32768	2½	262144	4096
"	lupine	32768	5	65536	4096
"	corn	131072	1	524288	4096
KOH	pea	256	4	512	128
"	lupine	128	4	256	128
"	corn	64	1	128	64
NaOH	pea	128	3	256	128
"	lupine	64	1	128	128
"	corn	64	2½	128	64
Na_2CO_3	pea	256	12	512	32
"	lupine	128	8	256	32
"	corn	64	12	256	32
$NaHCO_3$	pea	16	3	128	16
"	lupine	16	20	32	16
"	corn	8	1	16	8

* $n/171$ was the highest concentration we were able to obtain, and both the lupine and the corn withstood this readily in a quantity of 25^{cc} and upwards.

In Table XX is a recapitulation showing the quantities of solution and the concentration which the seedlings just endured. A comparison is also made between the liquid test and the sand test. In columns 3, 5 and 6 is given only the denominator of the fraction whose numerator is n. In column 4 is recorded the number of cubic centimeters in which the radicles just lived, and in column 5 is given the highest concentration the seedlings could withstand in a quantity of 25^{cc} or upwards.

It should be remembered always that the test applied to decide life was *further growth* in water after the seedling was taken from the test solution. Column 4 gives the number of cc. in which the radicle just lived at the concentration opposite in column 3. In column 6 is given the concentration the seedlings would endure when sand was present; the amount of solution to each radicle was $3\frac{1}{2}$ to 6^{cc}, and the amount of sand about 5 to 8^{cc}.

A comparison between columns 3 and 5 in Table XX shows the variation due to *quantity* of solution. (It ought to be mentioned that when the experiments were arranged, the liquid used in all the vials of different size was taken from the same preparation, so that practically every element which might affect results was eliminated.) It may be seen further that a comparison of these results with those of Heald shows some difference of figures. No attempt is here made to reconcile these differences because a general *actual* toxic limit is not possible to obtain.

Column 6 shows clearly that the presence of sand affects the characters of the solution in regard to toxicity. In dilute solutions it reduces it enormously; in strong solutions not nearly so much. Though the figures opposite $NaHCO_3$ are close, yet if working with more closely graded quantities and concentrations slightly different results from those given might be expected.

The problem of soils, examined from this point of view, presents a very complicated question, from the fact that several substances enter into the composition of soil water. It is then a problem of permutations and combinations of $(n+1)$ substances, making factorial n cases for each combination. And, since the amount of each may vary from an insignificantly small to a predominating quantity, the number of problems from this side is at once enormous; and if the theory of dissociation be admitted into the proposition, the problem is still more complicated. There is then the possibility of ion effect, coupled with electrical forces, augmented or neutralized by the presence of a number of different ions.

In order to learn something of the differences in effect between fine and coarse sand, solutions of $CuSO_4$, $n/8192$, HCl, $n/512$, H_2SO_4, $n/512$ were compared with the following results: more growth was permitted in fine sand with $CuSO_4$ but, on the other hand, considerably more growth was permitted with coarse sand when HCl and H_2SO_4 were used. In all the experiments these were the general results, H_2SO_4 presenting the most marked character. One explanation of this may be that because of the greater surface, the fine sand would hold mechanically more of the solute when in very dilute solution

with heavy kations; whereas with stronger solutions and lighter kations, the centers of mass attraction being fewer, and the force consequently greater, the result might be that more light kations would be held by a mere force of attraction.

Two forces seem to be exerted, one by virtue of the surface exposed (surface tension so-called), and the other by virtue of the mass (gravitation). When the former encounters a substance which is attracted more by surface tension than it is by the mass, then the fine grains will exert a predominating influence upon the solute. When the latter encounters a substance which is more affected by mass than by surface tension, then the coarse grains will exert a predominating influence. At all events, we have the facts derived from the experiments, and it seems but fair to borrow explanations from the physics side of the question.

In the case of corn seedlings, an aquatic fungus frequently developed if the plants remained in the liquid for a few days. The tendency to curl has also been pointed out.

An investigation into the cause of the fungus growth showed that, near the root tip, some organic substance exuded from the plant. This substance contained some organic matter which acted, on heating, like sugar. When evaporated on a clean cover-glass, a syrup-like substance remained. For a further test, seedlings were allowed to send out aerial roots in a moist chamber under a bell-jar, and the root tips were then cut away at a point about 2^{mm} from the apex. In three hours a drop of clear liquid, about 2^{mm} in diameter, appeared at the cut end of the root. This drop, upon examination, proved to contain a large proportion of organic matter of a sugary nature, and a small quantity of ash of an alkaline reaction.

There is no doubt that this substance forms a nutritive material for fungi. Nor is it confined to the root tip, but may be found 20^{mm} or more from the tip. This was quite apparent in the sand cultures. Upon taking the corn seedlings from the culture media, whether sand or liquid, if the plant had not been killed, the liquid adhering to the tips and elsewhere was of a "glairy" consistency, slightly like white of egg, or like syrup.

The suggestion is here offered that the reason corn is enabled to withstand stronger solutions of acids and bases than some other seedlings, is in consequence of this secretion. Just what function this might serve is not known. At all events, a great loss to the plant, of organic food, may be suffered, if in cultivation the root-ends be bruised or broken.

In regard to the curling of the roots, it may be said that chemotropism has something to do with it, but just why it turns this way or that, in a solution where the forces are equally

distributed on all sides, is not easy to say. Such a curling is often seen in the radicles of corn seedlings grown in water or in the ordinary water-culture media. Cameron (l. c.) gets over the difficulty by saying: "They tended to curl up in an apparent effort to leave the solution, seeking a more congenial environment." This is assigning to plants a will-power we were not aware they possessed.

Summary.

Quantity of solution has an important bearing upon its power to affect the radicle; and rate of diffusion proves also to be of some significance.

Non-chemical* bodies retard very materially the activity of the solute in bringing about death to the radicle. In some instances the toxic effect was reduced 32 times by the mere presence of pure sand. The mere presence of the walls of the glass vessel has a perceptible effect in holding a substance mechanically; and the shape of the vessel is also not without some effect.

The action of the solute upon the radicle is very probably a chemical one.

There is no support to the theory of electrolytic dissociation from the physiological side. In fact, certain substances present phenomena which indicate opposition to it.

Both the carbonate and the bicarbonate, if they dissociate at all, do so in such a manner as to result in a chemical action upon the water, forming a hydroxide as one of the products.

Carbonic acid is of extremely low toxic power, killing the radicle of the pea at $n/342$, but not the corn nor the lupine at any concentration which it was possible to obtain ($n/171$).

Agricultural College, Michigan.

* After this paper was written, an abstract of a paper by True and Oglevee bearing, in part, on a similar line of investigation, appeared in Science Mar. 11, 1904, p. 421.

TOURMALINE FROM SAN DIEGO CO., CALIFORNIA.

ART. XLIII.—*Tourmaline from San Diego County, California;* by DOUGLAS B. STERRETT. (With Plate XXIV.)

THE tourmaline crystals to be described in this article are from Damaron's Ranch, four miles northwest of Mesa Grande, San Diego County, California. A representative collection of over one hundred and sixty specimens given to Prof. Penfield by Mr. Ernest Schernikow of New York, and deposited in the Brush collection of the Sheffield Scientific School, was used for most of the investigation; which is here directed chiefly toward the study of crystal form. Additional notes were obtained from a brief examination of the collection on exhibition

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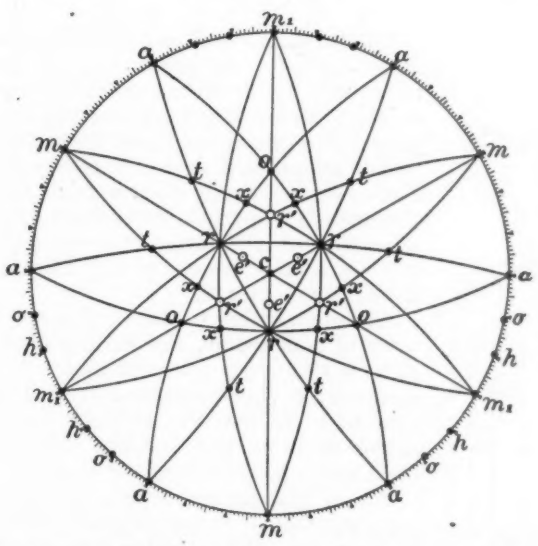


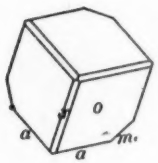
at the Natural History Museum, New York, loaned by Mr. Schernikow, and from the choicest crystals in Mr. Schernikow's possession. The crystals have evidently come from a pegmatite vein, as they are often associated with large quartz and feldspar crystals and bunches of lepidolite mica. They far surpass the crystals of Paris and adjoining localities in Maine in perfection of crystallization, and those of Haddam Neck, both in size and crystallization. It is also probable that no other locality produces stones with more varied and beautiful colors.

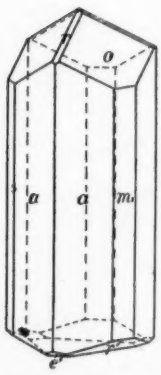
Many crystals are of gem quality, and according to "The Mineral Industry,"* $15,000 worth of gems were produced from this locality during the year 1901, and Mr. Schernikow places the value for 1903 between $40,000 and $50,000.

The number of forms found on the crystals is not great and only those common to tourmaline have been observed, a list of which is given in the accompanying table and shown in stereographic projection in fig. 1.

Prisms.	Upper end.	Lower end.
a $(11\bar{2}0)$	c (0001)	c' $(000\bar{1})$
m $(10\bar{1}0)$	r $(10\bar{1}1)$	r' $(01\bar{1}\bar{1})$
m_1 $(01\bar{1}0)$	o $(02\bar{2}1)$	e' $(10\bar{1}\bar{2})$
σ $(12\bar{3}0)$	t $(21\bar{3}1)$	
h $(14\bar{5}0)$	x $(12\bar{3}2)$	

2





The forms σ and h could not be accurately determined, for the prism faces of the crystal on which they were measured were badly striated. Reflections were obtained from thin glass strips glued on these faces, and gave results approximating to the above symbols. The character of the other crystals measured was such as to permit very satisfactory determinations of the forms enumerated, but it has not seemed necessary to publish a list of the angles measured.

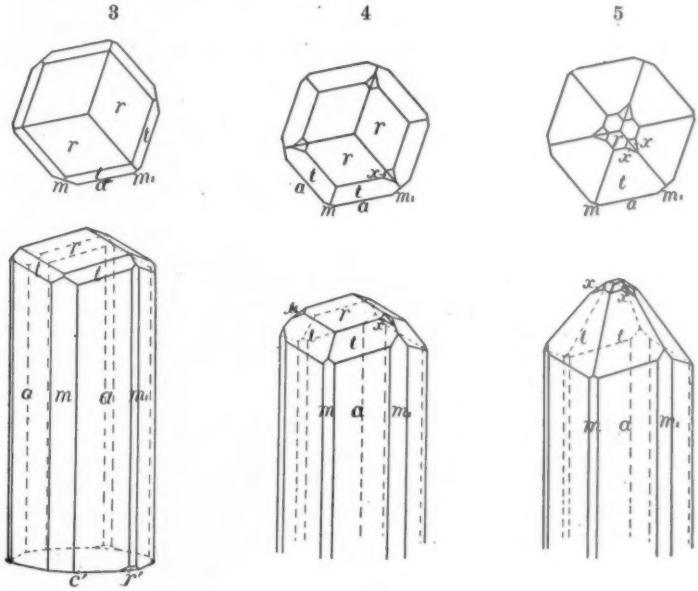
Although owing to the hemimorphic character of tourmaline, the three r faces above form a triangular pyramid and not, strictly speaking, a rhombohedron, it will be convenient to refer to this and similar forms as rhombohedrons, and for like reason to call the t and x faces scalenohedrons.

All of the figures drawn in clinographic projection have the antilogous end up, i. e., that pole which on cooling is positively electrified, and when tested by the Kundt method attracts sulphur. The crystals all follow the general rule, that the end with the steeper forms is the antilogous pole.

For a single locality the crystals show an unusual diversity of habit and color, and in describing them it will be convenient to divide them into types. In the first type the rhombohedron o forms the principal termination above, sometimes with a replacement of its edges by r, as shown in fig. 2. The lower

* Published by the Engineering and Mining Journal of New York.

termination when present is made up of c', r' and e' variously developed. The crystals show considerable variation in length; as a rule they are slender and the prisms are generally striated. No. 2 of the plate has been broken at the lower end and does not show its full length; while No. 3 and fig. 2 represent doubly terminated crystals. The colors are transparent pink or green throughout, or combinations of pink above and green below.



A second type is represented by figs. 3, 4 and 5, which are especially interesting because of the development of the scalenohedron t, and on some crystals a second scalenohedron x shows slight development. The lower termination when present generally consists of the basal plane and subordinate r', as shown in fig. 3. Most of the crystals are pink or rose color throughout; some are dark enough to be classed as rubellite; occasionally they are light green at the lower end. Some of the finest pink gems are cut from crystals of this type.

It is very unusual to have tourmaline crystals terminated as in fig. 5 by a large development of a scalenohedron. The brown tourmaline from Gouverneur, N. Y., shows a similar develop-

ment, but the scalenohedron is a steeper one, u (32$\bar{5}$1), and fig. 6 is here introduced for comparison.

The features of a third type are the number of prism forms and two bases, generally well developed, with subordinate rhombohedrons o, r' and e', as shown in fig. 7. The crystals are, as a rule large; 7^{cm} high and 3^{cm} thick not being uncommon. The development of the rhombohedrons o and r' sometimes varies, with a consequent variation of the base; this forms a connecting link with the first type; for some crystals have only a small base with large o faces; if c were to fail entirely, the crystal might be considered of the first type.

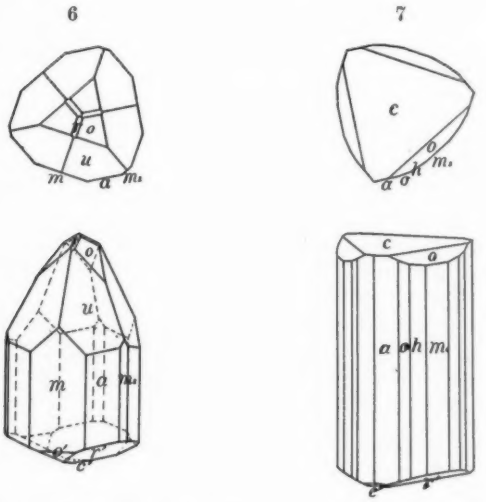


FIG. 6. Brown tourmaline from Gouverneur, N. Y., with scalenohedral development for comparison with fig. 5.

These crystals display a most remarkable variation of color, often of a quality unsurpassed by tourmaline from other localities. As an example, a description of one of the numerous crystals in Mr. Schernikow's collection will answer. Beginning with the lower end there is a layer of fine green; above this, bluish green fading into light rose color; then sea-green passing into smoky brown or brownish green; on this comes a cap of dark pink, appearing scarlet by reflected light. All of these colors, with the exception of the smoky brown, are trans-

parent and clear. One crystal has a lilac-colored band, formed by the blending of pale blue and pink layers.

Crystals of a fourth type are often short and stout, terminated by basal planes and rhombohedrons. The prism zone is made up of deeply striated faces; or more properly speaking, layers of small crystals. The terminations consist of the bases and rhombohedrons, *o*, *r*, *r'*, and *e'*. The termination at the antilogous pole more often fails, and is generally rough and much corroded. Fig. 8 is a basal projection of the analogous pole of a distorted crystal of this type. These crystals commonly have a pink or white middle and green layers or cap at the ends. The corroded end is a dark semi-transparent green; while the other is transparent grass- or pale apple-green. One crystal has a cap of pale sulphur-yellow color. Other exceptions are white crystals, faintly tinted with pink and containing perfectly colorless portions.

8

Crystals of a fifth type have a black exterior or shell; generally less than a millimeter thick. Within there is a core of light colored material, green, pink or whitish. When the terminations are present, they are found to be *c*, *o* and *r* above with *c'* and *r'* below.

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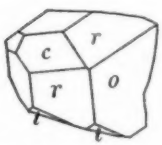

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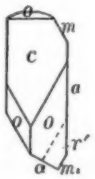
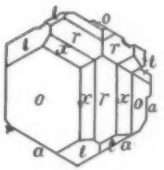


11

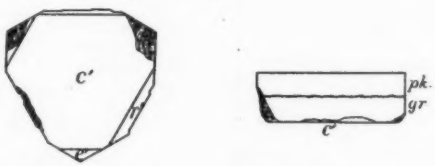


All of the crystals with an olive- or pistache-green color are included in a sixth type. Some are slender, as No. 1 of the plate; these are olive-green passing into brownish green at the upper end. Others vary up to 5^{cm} in thickness and often have a silky luster with pistache-green color. The upper termination of *o* and *r* sometimes appears, though the ends are generally etched and corroded. Crystals of all sizes, from that of a needle up, are found penetrating large crystals of quartz and feldspar.

Figures 9, 10 and 11 are end views of crystals so distorted as to be difficult to put under any special types. In fig. 9 the directions of the prism faces are not preserved on the crystal, so the outline was drawn as nearly as possible like the original.

Fig. 10 is the same as No. 9 of the plate and is a doubly terminated crystal, the dotted line representing the development of one of the lower rhombohedral faces. The crystal shown in fig. 11 was loaned by Mr. Schernikow for examination and is unusual owing to the development of x and t modified by the presence of an o face. One t face (on the upper right hand side) is divided into two parts by a deep striation. Fig. 12 is an end and side view of a section cut from the lower end of a pale pink crystal with green cap. A natural basal plane c' forms one surface of the section, and is modified by small r' and e' faces. The intensity and thickness of the two colors are nearly equal and an interesting feature is that on looking through the section in the direction of the vertical axis, the two colors complement one another and a nearly white light is transmitted. Another transverse section with an oil-brown core and rose-colored exterior, each of the finest quality, gives a good illustration of the internal strain crystals may be subjected to, owing undoubtedly to variations in chemical composition; for in most positions under the polariscope, it gives a biaxial interference figure. Some crystals have internal striations parallel to the vertical axis, ending in little pits or etchings on the terminal faces, and when coarse, often partly filled

12



with clay. When these striations are fine and numerous, the crystals may be cut "en cabachon," and give most excellent cat's-eye effects.

In conclusion the writer wishes to express his sincere appreciation of the constant assistance and advice of Prof. S. L. Penfield in the preparation of this article; and also to acknowledge the courtesy extended to him by Mr. Schernikow.

DESCRIPTION OF PLATE XXIV.*

1. Olive-green crystal of the sixth type.
2. Transparent, sea-green, with clear pink cap; first type.
3. Crystal with colorless middle part and pale pink ends; first type.
4. Transparent throughout; lower half pale green, upper half pink; second type.
5. Pink with cap of exquisite rose color; second type, same as figure 4.
6. Small pink prism penetrating the end of a quartz crystal.
7. Rough sea-green crystal passing abruptly into a pink cap at the upper end.
8. Distorted and flattened crystal of green color fading into pale pink at the upper end.
9. Distorted crystal shown in basal projection in figure 10; sea-green color with an almost colorless cap slightly tinted with pink.
10. Cat's-eye cut from a crystal with internal striations, which can be seen running horizontally through the stone.
11. Section cut from a crystal with a smoky brown core surrounded by a light greenish brown layer and pink shell.
12. Rounded bunch of lepidolite mica with albite adhering to the lower part.
13. Pink crystals coated with a crystalline incrustation of cookeite enclosing quartz and lepidolite.
14. Section broken across a crystal with a dark brown core and lighter colored shell.
15. Bent crystal; the lower half is light pink passing into a pale green middle and back to pink at the upper end. Where the crystal had evidently been fractured by the bending, it has been healed by bands of fibrous tourmaline with silky luster.
16. A crystal of the fourth type. Grass-green cap at the upper end (analogous pole in this case), with white middle and corroded dirty green cap at the lower end.
17. Group of transparent pale pink crystals; analogous ends free and terminated by c' and subordinate r'.

* Nine-tenths natural size.

ART. XLIV. — *The Limit of Error in the Volumetric Determination of Small Amounts of Gold;* by RALPH N. MAXSON.

[Contributions from the Kent Chemical Laboratory of Yale University—CXXVII.]

IN a former paper from this laboratory, Gooch and Morley* established the accuracy of a method for the determination of small amounts of gold, based upon the reaction

$$AuCl_3 + 3KI = 3KCl + AuI + I_2.$$

Recently the attempt has been made by Rupp† to show that this method is inaccurate, and to bring forward a process based upon the reduction of gold by standard arsenious acid, and titration of the residual arsenious acid by standard iodine. In a study of these two methods,‡ I have verified the results obtained by Gooch and Morley, but have been unable to determine similar amounts of gold with even approximate exactness by the method of Rupp.

More recently,§ Rupp has disclaimed accuracy for his method when applied to amounts less than a few milligrams, and proceeds to discuss the absurdity of attempting to determine volumetrically tenths and hundredths of a milligram of material, however accurate the method may be—and this in the face of his statement, in his own previous paper, of volumetric results carried to thousandths of a milligram.

While quite in agreement with Rupp so far as to admit the absurdity of attempting to determine amounts of material measured in tenths and hundredths of a milligram by means of N/2 arsenious acid, as did Rupp in three out of the six determinations upon which he rested his process, I take the view, that with properly made standard solutions of suitable dilution, it is quite possible for a skillful analyst to determine tenths and hundredths of a milligram of material.

By the use of approximately N/100 iodine and thiosulphate, Gooch and Morley got results with a mean error of 5/100 milligram between extremes of +3/100 mg. and −10/100 mg. in twelve determinations, a single small divided drop of the iodine solution and of the thiosulphate solution being sufficient to produce an immediate reaction with starch, and a bleaching of the starch color, respectively.

When using N/1000 solutions of iodine it was necessary to add to the volume used $0{\cdot}1^{cm^3}$ of iodine, in order that the first small drop of gold should bring out the starch reaction. This was a perfectly definite correction and was equivalent to 1/100 mg. of gold.

* This Journal (4), viii, 261, 1899.
† Ber. Dtsch. Chem. Ges., xxxv, 2011.
‡ This Journal (4), xvi, 155, 1903.
§ Ber. Dtsch. Chem. Ges., xxxvi, 3961.

With N/1000 solutions and with the application of this correction, ten experiments gave a mean error of less than 4/1000 mg. between extremes of +2/100 mg. and −29/1000 mg.; while in another series of experiments in which the start was made with pure gold foil, dissolved in chlorine water and treated by a process carefully described, the average error of fourteen determinations was +2/1000 mg. between extremes of +1/100 mg. and −8/1000 mg. This is not theory: it is experiment. Here are volumetric solutions capable of showing 1/100 mg., or less, of gold. Is it any more absurd to determine gold in this manner than to weigh that element upon an assay balance sensitive to 1/100 of a milligram? To be consistent, Rupp should include all processes, gravimetric as well as volumetric, in his sweeping declaration.

The fact that large percentage errors occur in certain determinations made by Gooch and Morley, upon small amounts of gold, is again made the subject of criticism by Rupp.

As I have previously stated, every analytical process has a certain inevitable error, and because of this fact as we approach the limit of accuracy of the process the percentage error will increase rapidly. This increase can, however, under no circumstances be considered a reason why small quantities of substances should be disregarded in analysis, either volumetric or gravimetric. Because the ordinary analytical balance is sensitive only to 1/10 or 1/20 mg. is no reason for declining to weigh tenths or twentieths of a milligram, although the percentage error in weighing such amounts may be very large.

Besides these wholly unreasonable criticisms, reference is made by Rupp to some matters of scientific fact, and to these I next propose to give attention.

To Rupp's statement that with dilute solutions the starch indicator is no longer reliable, it is sufficient to reply that experience has shown that one small drop of N/100 iodine solution developes the starch color at once, in solutions of the volume and concentration described; and if N/1000 solutions be used, a perfectly definite, and not excessive allowance of 0·1^{cc}, equivalent only to 1/100 mg. of gold, is all that is needed.

Further, Rupp claims that the decomposition of aurous iodide is the greatest error of the process of Gooch and Morley, and refers to the handbooks of chemistry to substantiate this opinion. No handbooks are known to me which discuss the deportment of aurous iodide under exactly the conditions of this analytical process, but a study of the reaction, of which I made mention in a former paper,* showed that aurous iodide possesses stability sufficient for the purposes of the analytical process.

* Loc. cit.

I have, however, thought the matter of sufficient interest to warrant further investigation concerning the deportment of this salt under more varied conditions.

The method employed to determine the rapidity with which the aurous iodide decomposes was as follows: A measured quantity of a standard gold solution was drawn off into a beaker and diluted to the required volume. To this was added the necessary amount of a solution of pure and specially prepared potassium iodide, starch was added, and the freed iodine immediately treated with N/100 thiosulphate solution, but only to the rose tint, so that, as in the actual analysis, there might be no decomposing action due to an excess of thiosulphate upon the aurous salt.

The time was noted and the mixture allowed to stand until the iodine freed by the decomposition of the aurous iodide had brought the color of the liquid to an ordinary starch blue. The data obtained in this manner are shown in the following table. The gold solution used contained ·00048 g. of metal to the cubic centimeter.

No.	Gold grm.	KI grm.	Volume before the addition of thiosulphate. cm^3	Time in minutes necessary to give blue color.
1	0·0144	0·20	50	19
2	0·0144	0·20	50	47
3	0·0144	0·20	50	95
4	0·0144	0·20	50	150
5	0·0144	0·20	50	115
6	0·0144	0·20	50	82
7	0·0144	0·20	50	50
8	0·0096	0·08	50	17
9	0·0096	0·08	50	95
10	0·0096	0·08	50	28
11	0·0096	0·08	50	78
12	0·0096	0·08	50	18
13	0·0096	0·08	50	30
14	0·0096	0·08	50	36
15	0·0096	0.08	50	32
16	0·0048	0·05	50	45
17	0·0048	0·05	50	168
18	0·0048	0·05	50	25
19	0·0048	0·05	50	48
20	0·0048	0·05	50	43
21	0·0024	0·05	50	95
22	0·0024	0·05	50	105
23	0·0024	0·05	50	135
24	0·0024	0·05	50	none in 3 hours
25	0·0024	0·05	50	none in 3 hours
26	0·0014	0·01	35	130

It may be seen from these results that the decomposition of the aurous iodide under the conditions is comparatively slow, although potassium iodide was present in large excess. In these experiments the coloration ran through various gradations from pink to blue, as the starch used, in common with most specimens, had suffered hydrolytic change, the pink color indicating, of course,* the incipient excess of iodine, and not under-titration as Rupp has stated.

As I have previously shown, a complete determination by the method of Gooch and Morley can be easily accomplished in ten minutes; the maximum time actually necessary for the completion of the titration *after* the formation of the aurous iodide need not exceed four minutes. As can be seen from the experiments tabulated above, the minimum time required for the incipient decomposition of the aurous iodide was seventeen minutes. In no case did decomposition take place immediately, although potassium iodide was present in large excess. It is to be especially noted that these experiments begin where the analytical process ends, so that the probability of any iodine being freed by a too rapid decomposition is rendered yet more remote. The facts, then, afford absolutely no foundation for the statement that the decomposition of aurous iodide is an inherent source of error in the method of Gooch and Morley.

Concerning the accuracy of the method proposed by Rupp it is unnecessary to speak further, since Rupp now disputes the desirability of estimating less than the milligram; but to the reduction of gold chloride by arsenious oxide, the reaction used by Rupp, it is necessary to recur. Rupp states that the process of reduction goes on in acid solution. As I said in a former paper, I have been unable to effect the precipitation of the gold when free acid is present, but after the addition of acid potassium carbonate, reduction takes place. Rupp added to his solution of gold chloride containing hydrochloric acid, 10^{cm^3} of nearly N/2 solution of arsenious oxide. It is to be supposed that this solution of arsenious oxide was made, as usual, by dissolving the oxide in acid potassium carbonate. The question arises as to whether Rupp did not have enough acid carbonate in his arsenic solution to neutralize the free acid. The fact that the gold was precipitated, and within ten or fifteen minutes, points strongly, according to my experience, to an alkaline condition of the solution. So, if to heat a solution of acid potassium carbonate upon the water bath, under the experimental conditions, brings about the formation of an iodine-binding carbonate, and is indeed an error as Rupp says, it would seem that Rupp makes that error. But was it an error? It has seemed worth while to investigate this point.

* See Hale, this Journal (4), xiii, 390, 1902.

A N/10 arsenic solution was prepared as usual with the aid of 20 grams of potassium acid carbonate to the liter. Twenty-two cubic centimeters of this solution were drawn off and titrated with an approximately N/10 iodine solution in the usual manner. Four lots of this arsenic solution of 22^{cm^3} each were then carefully drawn off and heated upon the steam bath for thirty minutes, and when cool were titrated against the above mentioned iodine solution. The volume of the solutions used in these experiments was in all cases approximately 75^{cc}. The results obtained are given in the accompanying table.

Standard As_2O_3 taken. cm^3.	Iodine used to titrate at once. cm^3.	Iodine used to titrate after heating ½ hour on the water bath. cm^3.
22·0	22·08	22·10
22·0	22·07	22·08
22·0	22·08	22·09
22·0	22·07	22·08

These figures show conclusively that acid potassium carbonate in solution of the concentration used in these experiments, 0·44 grms. in a volume of 75^{cc}, does not in thirty minutes heating upon the water bath undergo such change as to cause it to absorb an appreciable amount of iodine in the following titration. Just what the effect may have been in Rupp's experiments cannot of course be determined in the absence of knowledge in regard to the acidity of his gold solution, and the alkalinity of his arsenic solution.

In conclusion it is obvious that the criticisms made by Rupp are not warranted by the facts. While, as its author now concedes, the method proposed by Rupp is not to be considered of value for the determination of small amounts of gold, all the evidence goes to show that the process of Gooch and Morley is accurate, and in the hands of a skillful analyst, adapted to the estimation of minute quantities of gold.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *Hydrates in Solution.* — It has been known for some time that many inorganic salts give abnormal results in the lowering of the freezing points of their comparatively concentrated aqueous solutions. They show in dilute solutions depressions of the freezing point which correspond to their ionization as determined by electrical conductivity, but when a certain degree of concentration has been reached the depression of the freezing point is abnormally great in most cases. H. C. Jones and his co-workers have made an extensive study of this matter, and it has been found that all but nine of the forty-nine substances experimented upon showed a minimum in the freezing-point curve; that is, the effect of the substance in lowering the freezing point gradually diminished as the concentration increased—on account of diminished ionization—and then the abnormal increase of effect occurred to such an extent that the curve showed a minimum point. Even where the freezing-point curves did not show a minimum, there was an abnormal depression of the freezing point in nearly every case with concentrated solutions. It was found also that those substances which crystallize out of solution with the larger number of molecules of water of crystallization give the greatest molecular lowerings of the freezing point of water in concentrated solutions. The boiling-point curves, as far as they have been worked out, also show a minimum, but this occurs at a greater concentration than in the corresponding freezing-point curve.

From the results of this work, the important conclusion is reached that in concentrated solutions a part of the solvent is combined with the dissolved substance, and such solutions are, therefore, more concentrated than they would appear from the amount of dissolved substance present in them. This view explains the abnormal behavior of concentrated solutions in a very simple and satisfactory way; for it is difficult to imagine that substances should crystallize with water of crystallization, unless they were capable of combining with this water while in solution. If further work confirms this new explanation, a serious objection to the ionic theory of solutions will be removed.— (Jones and Getman) *Amer. Chem. Jour.*, xxxi, 303. H. L. W.

2. *A Microscopical Method of Determining Molecular Weights.* —This interesting method, described by George Barger, of King's College, Cambridge, England, depends upon the increase or decrease in size of alternate drops of two solutions in a closed capillary tube. One of the solutions is prepared from a substance of known molecular weight, while the other contains a known amount of the substance whose molecular weight is to be determined. When the two solutions contain the same number of molecules in a given volume, the vapor tensions will be equal and

the drops will not change in size, but if one of the solutions is stronger in this respect, its drops will increase in size at the expense of the other. The method then consists in finding a known solution of the same vapor tension as the known one by microscopic measurement of the drops. It is not necessary that the solvent used should have a constant melting point or a constant boiling point, hence impure solvents, such as ether saturated with water, 90 per cent alcohol or 80 per cent acetic acid can be used successfully. The solvent should not be too volatile, on account of the difficulty of manipulation, and, on the other hand, if the solvent is not sufficiently volatile, the experiment takes too long. The details in regard to the application of the method need not be given here, but it may be observed that the process has been tested with a great variety of substances with satisfactory results.—*Jour. Chem. Soc.*, lxxxv, 286. H. L. W.

3. *Rubidium-Mercuric Double Salts.* — GROSSMANN has prepared the double salts

$$2RbI \cdot HgI_2,$$
$$RbI \cdot HgI_2,$$
$$2RbSCN \cdot Hg(SCN)_2,$$
and $$RbSCN \cdot HgSCN,$$

and also a pyridinium-mercuric cyanide-thiocyanate,

$$(C_5H_6N)SCN \cdot Hg(CN)_2.$$

From these results it appears that rubidium iodide forms a much less extensive series of double salts with mercuric iodide than is the case with cæsium iodide, for with the latter five double salts are known. The double thiocyanates under consideration correspond exactly to the cæsium-mercuric salts described by Wells and Bristol, except that one of the latter, $2CsSCN \cdot Hg(SCN)_2 \cdot H_2O$, contains water; hence there is no evidence in this case of a more extensive series of salts with cæsium than with rubidium. The pyridine compound is an example of the combination of mercuric cyanide with many kinds of salts.—*Berichte*, xxxvii, 1258. H. L. W.

4. *Zirconium Tetra-iodide.* — By acting upon metallic zirconium or upon zirconium carbide with hydrogen iodide at elevated temperatures, STÄHLER and DENK have obtained the tetra-iodide ZrI_4 in the form of a sublimate, consisting of a reddish brown, crystalline powder which fumes strongly in the air and reacts violently with water and acids. This substance is entirely different from the product, supposed to be this compound, obtained by Dennis and Spencer several years ago, which consisted of white crystals that were not decomposed by water or dilute acids. It appears, from the close analogy known to exist between the compounds of titanium and zirconium, that the composition of the white compound was incorrectly determined.—*Berichte*, xxxvii, 1135. H. L. W.

5. *Use of the Thermal Junction in the Ultra-Violet.* — A. PFLÜGER shows that it is possible to detect the heat of spectral lines in the extreme ultra-violet by means of a Ruben's thermal junction and the throw of a delicate galvanometer. The strong lines of cadmium, zinc, aluminium, etc., gave deflections of many hundred scale divisions, and even the finer lines of these metals gave deflections from 20 to 100 scale divisions.

It is shown that the energy distribution in these ultra-violet lines of the metals, with the exception of magnesium and iron, is strongest below wave length 260$\mu\mu$, and in a region where the ordinary photographic plate fails to register. The aluminium line at 186$\mu\mu$ shows a very strong energy radiation. The author found it useful to use single breaks of the primary circuit and to notice the first deflection of the galvanometer. The thermal junction was enclosed in a vacuum to avoid currents of air. The table of distribution of energy in the spark spectra of metals shows that the energy of radiation of the ultra-violet lines is in general far greater than the ultra-red lines. At first a quartz spectrograph was used, later a Rowland grating ruled on a fluor spar plate. Schumann's very short wave lengths also gave deflections with the thermal junction.—*Ann. der Physik*, No. 5, 1904, pp. 890–918. J. T.

6. *Internal Friction of Nitrogen.*—It is proved in the molecular theory of gases that the internal friction is independent of the density. Prof. S. W. HOLMAN has shown that the dependence of the viscosity upon temperature cannot be represented by a function of the absolute temperature with constant exponent, but that it increases the more slowly with the temperature the higher this latter is. In order to retain the theory of elastic spheres, STEFAN imagines that the mean free wave lengths at equal pressures increase with the temperature and the size of the molecule at the same time diminishes. One cannot at present verify this hypothesis by calculation. SUTHERLAND supposes a change in the attraction between the molecules is modified by a rate of collision, and he arrived at a formula which expressed under this hypothesis the ratio of the frictional coefficients at any two temperatures. A. BESTELMEYER takes up the measurement of the internal friction of nitrogen, according to the method used by Holman and arrives at the result that Sunderland's formula represents with great approximation the internal friction of nitrogen between 300° and −190°. The departure from the law at the temperature of liquid air indicates the beginning of a greater friction at lower temperatures.—*Ann. der Physik*, No. 5, 1904, pp. 944–995. J. T.

7. *Damping of Electrical Oscillations.* — The resistance of the electric spark assumes considerable importance in the subject of wireless telegraphy. The resistance is variously extended by different observers. BJERKNES estimates it at 11 ohms. BRAUN as 0·1 ohm. K. SIMONS measures the amplitude of electrical waves damped by spark gaps of increasing lengths, and concludes

that the resistance of a spark gap is so much the smaller, the greater the quantity of electricity in the discharge, and that within the limits of his observation the resistance of the spark gap increased with the length.—*Ann. der Physik*, No. 5, 1904, pp. 1044–1053. J. T.

8. *On the Compressibility of Solids*;* by J. Y. BUCHANAN, F.R.S.—The author has carried on a series of careful experiments for the determination of the absolute linear compressibilities, from pressures of 200–300 atmospheres, and at temperatures between 7 and 11° Centigrade, of the metals platinum, gold, copper, aluminium and magnesium. Tne method employed is that used by the author in determining the compressibility of glass in 1880, and developed earlier in connection with the deep-sea soundings made by the Challenger Expedition in 1875. Briefly stated, this method consisted in the use of a solid piezometer in which the rod of the glass to be experimented upon (57^{cms} in length) was inserted in a closely fitting tube of the same material; the two were fused at one end and at the other there was an empty space of some 3^{cms} between the end of the rod and that of the tube; a steel thermometer index was inserted at the end of the rod and the tube then sealed.

"Before the instrument was attached to the sounding line, the index was brought down by means of a magnet to rest on the end of the internal glass wire, exactly in the same way as if it had been the mercury column in a *maximum* and *minimum* thermometer. The instrument was then sent to the bottom, or to whatever depth might be decided on. During the descent the temperature of the glass, both inside and outside, fell with that of the water through which it passed, but as the contraction produced was the same on the wire and on the tube, there was no differential effect to be recorded by the index. On the other hand, the increasing pressure, as the instrument descended, affected only the outside tube, which it shortened. In contracting, it was obliged to pass the index, which was kept in its place by the internal wire. When the instrument was being hove up, the reverse process took place; the tube lengthened, and lifted the index clear of the internal wire by an amount equal to the lengthening of that portion of the tube. As the whole clearance produced by the expansion from the greatest depth did not exceed 1mm., its amount had to be estimated by the eye with the assistance of a magnifying glass."

The instrument of precision constructed in 1880 on the basis of the Challenger observations was essentially the same as that employed in the present research. The various parts of the latter instrument were made, however, of steel. The metals experimented upon were in the form of rods or wires and fitted into steel tubes passing into a central steel block. The ends of the rod or wire were closed with thick glass tubes kept in their places by open

*Read before the Royal Society of London, Feb. 25, 1904; from an advanced proof sent by the author.

steel caps; each tube was observed by a microscope with micrometer eye-piece. Details in regard to arrangements of the parts, the manometer employed, etc., will be found in the original paper. In regard to the progress of an experiment the author remarks:

"The effect observed and measured is the lengthening of the rod when the pressure is relieved. As the compressibility of solids is very small the highest pressures have been used which were found to be compatible with the reasonable persistence of the glass terminals; the usual pressure was in the neighbourhood of 200 atmospheres. Very few of the glass terminals stood over 300 atmospheres. The pressures actually chosen were as nearly as possible those at which the manometer had been compared with the 'Challenger' piezometer. The body under observation is in the form either of a rod or a wire. If it is in the form of a rod then it is fitted with wire ends of sufficiently small calibre to enable them to enter the glass terminals. During an experiment with a rod it contracts while the pressure is being raised, and expands again when the pressure is relieved. The steel tube which holds it, however, acts in the opposite sense: it expands while the pressure rises and contracts while it falls. If the two surfaces were perfectly smooth, one half of the change of length would be measured at the one end and the other half at the other end. As the surfaces are not perfectly smooth, this does not usually occur. Moreover the steel tubes are prolongations of the central steel block which holds them. The block is bored with holes at right angles to each other in the three principal directions. Consequently for a distance of about an inch and a half in passing through the block the rod is not supported at all. With the exception of this small portion, however, the rod is supported throughout the whole of its length by the steel tube. Now, although it is thus nominally supported equally throughout the whole of its length. we know that in reality this is pretty certain not to be the case. At some place, either in the right arm or in the left arm of the apparatus, the rod is sure to bear more heavily than in any other part. The contraction under pressure and the expansion under relief of pressure will then apparently take place as from this point as origin. Supposing this point itself to be motionless it is evident that the change of length measured at the two ends will be in the same proportion to each other as would be the arcs which they would describe if the rod were a lever oscillating on the point as a fulcrum. As there is no support at all at the centre this point must lie on one side or on the other of it and the motions of the ends must be unequal. But the fixed point of the tubular receiver is the central block; therefore any point in, let us say, the right-hand tube will, when pressure is being raised, move to the right, and on relief of pressure, retreat by an equal amount to the left. Consequently when we observe and measure the change of position of, for instance, the right-hand extremity

of the rod, when the pressure is relieved, that change of position is composed of two motions, the expansion of the part of the rod which lies between the right-hand extremity and the point in it whose motion with respect to the steel carrying tube is nil, along with the proper motion of that point. Similarly, when we measure the change of position of the left-hand end, it also is composed of two parts, the expansion of the part of the rod which lies between the left-hand extremity and the same point in the length of the rod where its motion with respect to the steel tube is nil, along with the proper motion of that point. But at the left-hand end the motion of expansion is to the left, and at the right-hand end it is to the right, while the proper motion of the position of the common point on the rod and on the tube is always in one direction, and in this case, to the left. Therefore the distance measured in the right-hand microscope is the expansion of the portion of the rod which lies to the right of the point on it which is motionless relatively to the tube *minus* the proper motion of this point: and the distance measured at the left-hand end is the expansion of the remainder of the rod *plus* the proper motion of the common point. Consequently the algebraic sum of the two motions measured is the expansion of the rod under the relief of pressure."

The following table gives a summary of the results obtained which are stated in full in six tables preceding. This final table is as follows:

Substance.	Year.	Atomic weight.	Density.	Compressibility.	
				Linear.	Cubic.
Platinum	1904	194	21·5	0·1835	0·5505
Gold	"	197	19·3	0·260	0·780
Copper	"	63	8·9	0·288	0·864
Aluminium	"	27	2·6	0·558	0·1674
Magnesium	"	24	1·75	1·054	3·162
Mercury	1875	200	13·6	1·33	3·99
Glass, flint	1880	...	..	0·973	2·92
" "	1904	...	2·968	1·02	3·06
" German	"	...	2·494	0·846	2·54

"In this summary the compressibilities of English flint glass and of the glass of which ordinary German tubing is made as well as that of mercury have been included for purposes of comparison. The compressibility of mercury rests upon a large number of observations made in the 'Challenger,' by which its apparent cubic compressibility was found to be 1·5 per million per atmosphere."

The author calls attention to the relation existing between compressibility and density, and remarks that a field for interesting research is here opened in which the method is capable of great refinement.

II. Geology and Natural History.

1. *United States Geological Survey.*—The following publications have been recently issued :

Folio No. 102. Indiana Folio, Pennsylvania ; by George B. Richardson. The Indiana quadrangle is made up of Carboniferous strata nearly all belonging to the Pennsylvanian series and containing workable beds of coal (Freeport). The two characteristic plains of the Allegheny Plateaus are almost unrecognizable in this part of Pennsylvania. The geologist will note the omission of structure sections.

No. 103. Nampa Folio, Idaho-Oregon ; by Waldemar Lindgren and N. F. Drake. The geological map of the Nampa quadrangle shows wide areas of dissected Tertiary lake beds together with extensive Quaternary gravels and recent flood plains. Tertiary basalt and rhyolite and Quaternary basalt occupy smaller areas. The lake beds of the Payette and Idaho formations once covered the whole district and this folio is in particular a study of the geographical conditions during the formation and partial destruction of beds of sand, gravel and clay with a thickness of 200 to 1000 feet. The characteristics of stream beds in arid regions are well shown by the Payette, Boise and Snake rivers.

No. 104. Silver City Folio, Idaho ; by Waldemar Lindgren and N. F. Drake. With the exception of Cretaceous ? granite, the formations represented on the Silver City quadrangle are Eocene, Pliocene and Quaternary. An early Tertiary epoch of erosion was followed by outbursts of rhyolite and basalt and the deposition of the Payette lake beds to a thickness of 2000 feet. A short period of erosion enabled the streams to cut to their present levels. The Idaho formation was deposited in the waters of a shallow lake during Pliocene time. The Snake River Canyon was cut during Miocene. Glassy basalts form the highest Tertiary beds and may have extended into the Quaternary. Terraces show the gradually deepening channel of the Snake River. The ore deposits at Silver City are fissure veins of post-Eocene age and cut through granite, rhyolite and basalt. Opals occur in vesicular cavities in the rhyolite and basalts.

No. 105. Patoka Folio, Indiana-Illinois ; by Myron L. Fuller and Frederick G. Clapp. Carboniferous strata of the Pennsylvanian series containing minor veins of coal are exposed in a small portion of the Patoka quadrangle. The most prominent and widespread formations are the glacial drift and the Wabash flood plains. The Illinoian stage is represented by an extensive series of lake deposits, gravel plains and ridges, and till sheets. The Iowan stage is represented by marl loess, while of the Wisconsin stage there remain small areas of dunes and terraces. The mineral resources of this region are coals and clays. Much valuable land has been reclaimed by draining and diking.

Bulletin No. 225. Contributions to Economic Geology, 1903.

S. F. EMMONS, C. W. HAYES, Geologists in charge. 527 pp. This report contains a series of fifty-one contributions from thirty-seven members of the Survey who have been engaged chiefly in economic work during the year. Brief introductory statements are also given on the investigation of metalliferous ores by S. F. Emmons and of non-metalliferous economic minerals by C. W. Hayes.

2. *The Atoll of Funafuti. Borings into a Coral Reef and the Results.* xiv + 428 pp., 6 pls., 69 figs. with 21 charts and geological maps. Published by the Royal Society.—Darwin believed that the history and origin of coral reefs must remain uncertain until a drill core could be obtained for a depth of at least 600 feet. Under the lead of Professor SOLLAS the Royal Society undertook to carry out this suggestion, and a committee, with Professor T. G. Bonney as chairman, was appointed to have general supervision of the project. Few scientific expeditions can match the Funafuti undertaking in determination and thoroughness. In 1896 Professor Sollas failed to attain a greater depth than 105 feet. The expedition of that year resulted, however, in valuable collections and in the construction of the most accurate and detailed chart yet made of an atoll. A study of the surface features and of the changes in elevation was made but few conclusions of general application were reached. Meteorological observations and magnetic surveys were also made. The expedition of 1897 resulted in a drill hole 698 feet deep, but was unsatisfactory owing to the small amount of solid core obtained. A detailed geological survey was, however, made of the atoll by Professor DAVID and Mr. SWEET. The third expedition, in 1898, succeeded in driving the boring down to 1114½ feet and obtaining about 384 feet of solid core. A hole was also bored into the lagoon to a depth of 245 feet. Slices for microscopic examination were taken longitudinally from the middle of each piece of rock. The core proved that the atoll was formed from the surface to the bottom of the bore of calcareous rock, chiefly composed of *Lithothamnion* and *Halimeda* as well as of reef-building corals. The lower part of the core seemed like a consolidated chalky ooze but was determined to be coral material converted into dolomite. A collection of living organisms on the seaward slope of the lagoon down to 200 fathoms was made for comparison with the dead organisms of the core rock. Professor David finds that the original foundation of the atoll is probably volcanic, that its shape has been modified by organic growth, winds and currents, that it is slowly enlarging its periphery, and that several oscillatory vertical movements of the shore have taken place in the immediate past. The Biology of the Reef-forming Organisms is discussed by A. E. FINCKH (pp. 125–150). Arranged in order of importance, Mr. Finckh describes the distribution, mode of occurrence, etc., of *Lithothamnion*, *Halimeda*, *Foraminifera*, *Corals*. Observations on the growth of reef-building organisms showed interesting results. For instance,

a mass of Halimeda increased 2¼ inches in height and 3¼ inches in thickness in six weeks! The drill cores were sent from Funafuti to England and were examined in microscopic sections by Professor JUDD and Dr. HINDE (pp. 167–361). The quantity of calcareous algæ is surprisingly large. Oolitic structure and stratification are absent and there is no admixture of deep water organisms, the same genera and species occur from top to bottom of the section. Extensive chemical and mineralogical changes have taken place in the rock since the corals were living, and these changes have been studied in detail by Professor Judd and Dr. CULLIS.

The reviewer is disappointed to find no discussion of the origin of coral reefs as illustrated by this typical atoll, yet the conclusion seems unavoidable that subsidence has been the chief cause of growth of the reef in this case. The workers in the Funafuti project deserve high praise for the conception of the scheme, for its successful execution under discouraging circumstances, and for the valuable scientific results obtained.

3. *A Revision of the Paleozoic Bryozoa;* by E. O. ULRICH and R. S. BASSLER. *Part 1. On the Genera and Species of Ctenostomata.* Reprinted from the Smithsonian Collections (Quarterly Issue) vol. 45, published April 11, 1904.—In this first part of the much needed revision of the Paleozoic Bryozoa, the authors discuss all the known species which can be referred to the order Ctenostomata. While the rather peculiar fossils so classified can not be proved to belong to this order, most of whose members are living species, the evidence seems to point strongly in that direction. The greatest objection is that the zoaria of the recent species are horny or membranaceous, while those of the Paleozoic forms were sufficiently calcareous to be preserved. The species, which number thirty-three, are arranged under five genera and three families: the Rhopalonariidæ (*Rhopalonaria*), the Vinellidæ, new family, (*Vinella*, *Heteronema*, gen. nov. *Allonema* gen. nov,), and the Ascodictyonidæ (*Ascodictyon*). It will be noticed that the family Ascodictyonidæ is here restricted to the typical genus and *Vinella* removed to a new family erected to include it and its allies. It is to be regretted that the authors have seen fit to insert here descriptions of a new genus and two new species, *Heteronema? contextum* sp. nov. and *Ptychocladia agellus* gen. et sp. nov. which are of so problematical a nature that they admit that the one may be a sponge and the other an alga or some peculiar type of Foraminifera. While there is reason for publishing descriptions of such peculiar organisms in order to get the opinion of other writers on the subject, it does not seem desirable to give new names, particularly new generic names, to fossils whose characters are so obscure that they cannot be definitely referred to any class or even kingdom. It is better to await the discovery of good material, as publication at this time only invites further revision. In addition to the description of the species, the paper

gives a good summary of the literature, and is well illustrated by four plates containing many figures of recent and Paleozoic Ctenostomata. P. E. R.

4. *An attempt to Classify Paleozoic Batrachian Footprints.* Trans. Roy. Soc. Can., 2d ser. vol. ix, Sec. IV, p. 109, 1903. *New Genera of Batrachian Footprints of the Carboniferous System in Eastern Canada.* Can. Rec. Sci., vol. ix, No. 2, p. 99, 1903; by G. F. MATTHEW, LL.D.—These articles are complementary to each other. The first takes a wider field of view than the second, viz.: the described Carboniferous tracks of America, supposed to have been made by Batrachian animals, and is an endeavor to classify these footprints according to their forms, and the number of toes represented. The author does not think the presence or absence of a tail mark or central groove between the rows of footmarks of the right and left limbs of general classificatory value, as some tracks which are closely alike in other respects are distinguished mostly by this marking; and the "tail mark" may be absent from one part of a trail and present in another.

A table is given at page 111 of the first paper in which the tracks of the Lower Carboniferous and the Coal Measures are arranged according to the number and the weight of the toe-impressions, etc.

Plates show some of these characteristic tracks, and give figures of new genera proposed. It is stated that no European footprints of Carboniferous age were considered in this classification and description of American forms.

5. *Geology;* by THOMAS C. CHAMBERLIN and ROLLIN D. SALISBURY. In two volumes. Vol. I, Geologic Processes and their Results. xix and 654 pp., 24 pls., with three tables of water analyses. New York, 1904 (Henry Holt & Company). — This volume, printed in clear type upon a heavy grade of paper, illustrated by numerous original drawings and photographs, both well selected and reproduced, possesses a distinctive character and fills a place not quite occupied by any other manual. The methods of treatment, as stated in the preface, bring especially to the front the methods of action and developmental aspects of the geologic agencies. Careful distinctions are drawn between those principles well founded on observed facts and others which have usually been as commonly accepted but which ultimately depend upon hypotheses as to the origin or internal nature of the earth. In the less certain departments of geological knowledge the method of multiple or alternative hypotheses is developed and the student shown the limitations of present real knowledge upon the subject. The first chapter consists of a preliminary outline on the field of geology, following which are chapters upon the work of the atmosphere, of surface and underground water, of snow and ice, structural geology, movements and deformations of the earth's body, extrusive processes and the geologic functions of life. The reputation of the authors in their several specialties is a sufficient

guarantee as to the depth and thoroughness of treatment, while in the chapter on the "Origin and Descent of Rocks," in which is presented an outline of the recently proposed quantitative system of classification, the authors have had the assistance of Prof. J. P. Iddings.

In the reviewer's opinion, the volume hardly supplants the manuals at present in use but rather supplements them, and from the somewhat philosophic and evolutionary cast would be most profitable to the student who has previously accumulated sufficient facts to feel the need of their coördination. It will be of chief value, therefore, to advanced students, to geological specialists, enabling them to get comprehensive outlooks over related fields, and to teachers of geology in general. The character of the volume should make it attractive also to the general reader of scientific tastes who wishes to follow the latest trends of geologic thought. J. B.

6. *The Mineral Resources of the United States for the Calendar year 1902;* DAVID T. DAY, Chief of Division of Mining and Mineral Resources. Pp. 1038, 8vo. U. S. Geological Survey, Washington.—This is the Nineteenth Annual Report of the series, and is in the octavo form which is most convenient for use. It gives the usual summary of the mineral production for the year, with detailed papers on specific subjects by different authors. The system now adopted of distributing the individual chapters in advance of the final volume, whenever such are ready, has the great advantage of bringing the material within reach of the public very promptly, while the complete volume issued later is invaluable for reference.

7. *Fragmenta Florae Philippinae;* by J. PERKINS, Ph.D. Fascic. 1; 66 pages imp. 8vo, Leipzig, 1904 (Gebrüder Borntraeger, price 4 marks).—Even before the pacification of the Philippines various projects were formed by Americans for the scientific investigation of the Islands. It was felt that the American occupation of this biologically rich archipelago not only offered to our investigators new opportunities but in a way imposed upon them certain obligations toward activity in the fresh field thus unexpectedly opened. In their enthusiasm some of those most eager to undertake this task little appreciated its difficulty. Biological areas are not changed by shifting political boundaries. The Philippines are and must always remain a part of the Old World. We have not in all America adequate literature or authentic specimens for a scholarly examination of the Philippine flora. To accumulate such material must be a matter of years of patient and critical labor. It is true that American energy, backed by the liberal support of the United States government, as well as by private patrons of science, could speedily bring together in our country Philippine collections more extensive than any which have resulted from the slower methods of Spanish or other foreign explorers, yet this is by no means sufficient. The Philippine flora possesses such a strong affinity with

the vegetation of the other Australasian islands, and, indeed, with that of continental India, that it can be studied intelligently only through comparison with types in foreign herbaria and by investigators familiar with Old World floras.

Under these circumstances, it was a wise decision of the Carnegie Institution to make a grant, not for the investigation of the Philippine flora in America, but to aid Dr. Janet Perkins in studying the subject in Berlin, where with access to numerous Old World types and with the counsel and collaboration of highly trained specialists on the Asiatic and Australasian floras, the work could be carried on in a far more scholarly manner. It is accordingly with great regret that we learn that this grant of the Carnegie Institution has not been renewed after the first year. Dr. Perkins, however, has continued her examination of the Philippine flora and a substantial installment of the results is now at hand.

The body of the present paper is occupied by an "Enumeration of some of the recently collected plants of Ahern, Jagor, Lober, Merrill, Warburg and others." In this copiously annotated list, including many diagnoses of new species and much critical synonymy, the *Leguminosae*, *Dipterocarpaceae*, *Anacardiaceae*, *Meliaceae*, *Pinaceae*, and *Taxaceae* have been treated by Miss Perkins herself, the *Symplocaceae* by Brand, *Acanthaceae* by Lindau, *Fagaceae* by von Seemen, *Typhaceae* by Graebner, *Orchidaceae* by Schlechter, *Palmae* by Beccari, *Myristicaceae*, *Pandanaceae*, and *Begoniaceae* by Warburg, and *Sapindaceae* by Radlkofer,—names which amply attest the critical nature of the work.

In a paper of such composite authorship uniformity can scarcely be expected, yet it is to be regretted that the diagnoses are partly in Latin and partly in English, and that the arrangement of the families is quite arbitrary, which in a publication as yet unindexed gives needless difficulty of reference. Among the plants discussed those of Mr. E. D. Merrill and of Dr. O. Warburg are the most numerous and interesting. It is to be hoped that Dr. Perkins may receive the encouragement and facilities in the continuance of her work which its scientific value so richly merits.

B. L. R.

8. *Botanical Publications by the Bureau of Government Laboratories at Manila.*—A series of pamphlets are being issued from time to time, under the auspices of the Department of the Interior, from the Government Laboratories in Manila, of which Mr. Paul C. Freer is Superintendent. Among these we note Nos. 6, 7 and 8, recently distributed, upon botanical subjects. No. 6 (36 pp.), by Elmer D. Merrill, describes new and noteworthy Philippine plants, and also discusses the American element in the Philippine flora. No. 7 (43 pp.), by Penoyer L. Sherman, Jr., discusses the gutta percha and rubber of the Islands, describing the various species and giving their distribution, with a map and numerous illustrations. Suggestions are made in regard to the

prospect not only of utilizing the natural supply, but also of introducing and cultivating foreign species.

No. 8 (193 pp.), by Elmer D. Merrill, gives a Dictionary of the plant names of the Islands with the botanical equivalents. There are two parts, in the first of which the local names and in the second the botanical names are made the basis of the alphabetical arrangement.

III. Miscellaneous Scientific Intelligence.

1. *Wilhelm Ostwald;* by P. Walden. 8vo, pp. 120. Leipzig, 1904 (W. Engelmann, price 4 marks). — Last December the friends and former students of Wilhelm Ostwald celebrated in Leipsic the twenty-fifth year of his doctorate. A special volume of the Zeitschrift für physikalische Chemie was issued on the occasion, and an account of Ostwald's life and work up to the present time. The volume of the Zeitschrift, containing nearly nine hundred pages, consists of contributions in German, English, and French from over thirty of his former students, coming from eight different countries.

Walden's account of Ostwald's life and work is exceedingly interesting and is told in a most entertaining manner. He was well qualified to undertake the work as he studied with Ostwald and is professor at Riga, where Ostwald was born and where he was professor for six years.

Ostwald was born in 1853, and as a boy and when first a student at Dorpat he was not particularly forward in his studies. When once started on his profession, however, his progress was extraordinary. After taking his doctor's degree in December, 1878, he immediately became an instructor in Dorpat. Two years later, in 1881, he was called to Riga as professor of chemistry, where he remained till 1887, and here in 1886 he received his first foreign student, S. Arrhenius, who proposed the theory of electrolytic dissociation the following year. He became professor of physical chemistry in Leipsic in 1887, a position which he still holds.

The first volume of his great 'Lehrbuch der allgemeinen Chemie' appeared in 1885 and from that time forward his literary work has been prodigious. He has written over twenty volumes representing fifteen thousand pages, besides several thousand reviews of scientific investigations and books. The Zeitschrift was started chiefly by him in 1887 and he has been one of the editors ever since.

As a teacher, he has been remarkably successful. His laboratory at Leipsic has been the center for physical chemistry since he took charge, and almost every branch of the subject has received its share of attention. Students have come to him from every civilized country. At the same time, he has carried on many investigations of his own. H. W. F.

2. *Changes in the Transparency of the Earth's Atmosphere.*—A circular letter has been issued, under the auspices of the U. S. Weather Bureau, having as its object the accumulation of data bearing upon the general diminution in the transparency of the earth's atmosphere noted by various observers during 1902, but which disappeared in 1903. Records are asked for "that will assist in defining the dates of beginning and ending, and the extent of this change in transparency. Such records may consist of photometric or photographic observations of the brightness of the stars; changes in the solar or stellar spectra; unusual prevalence of halos, large Bishop's ring, or haze; observations of heat received from the sun, as made with actinometers or pyrheliometers; observations of the polarization of the blue sky light and of scintillation of the stars. Undoubtedly this diminution and increase of transparency began and ended at different dates in different places, as the phenomena spread gradually over the world during the years 1902 and 1903; additional records are, therefore, desired in order to trace its progress."

Facts bearing upon this subject may be forwarded to Professor Cleveland Abbe at Washington, by whom the circular is signed.

3. *The Alpheus Hyatt Memorial Fund for Field Lessons.*—The report recently issued by the Trustees of the Hyatt Memorial Fund at Boston gives an interesting summary of the field work accomplished during the first year since the organization began. Superintendent Seaver states that 26 teachers from 9 schools have profited by the income of the fund and 2308 children have been taken to the seashore and country. The value of such field work as a part of the education of school children is obvious and it is gratifying to note that the money available produces so large a return. Contributions are asked for in order to increase the endowment; they may be sent to Mr. Stephen H. Williams, 24 Milk st., Boston.

4. *Altitudes in the Dominion of Canada;* by James White, Geographer. Geol. Survey of Canada, Ottawa, 258 pp.—Since 1894 Mr. White has been collecting and classifying data regarding elevations in Canada. Altitudes are given along railroads, rivers and in detail about the Great Lakes and the St. Lawrence. The present volume is the only publication containing this mass of fact and thus becomes a necessary reference book. Four profiles and a relief map of North America accompany the volume.

5. *Publication of the Earthquake Investigation Committee in Foreign Languages.* No. 15. Pp. 72 with eight plates. Tokyo, 1904.—This number is devoted to a discussion by F. Omori of the application of seismographs to the measurement of the vibration of railway carriages. It gives a detailed account of a series of practical experiments made upon the Government railways of Japan under varying conditions.

6. *Clarkson Bulletin, Vol. I, No. 2,* April, 1904. — This bulletin contains the announcement of the Clarkson School of Technology at Potsdam, N. Y., established in 1896. The second summer session begins July 6, 1904, and extends for six weeks.

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